

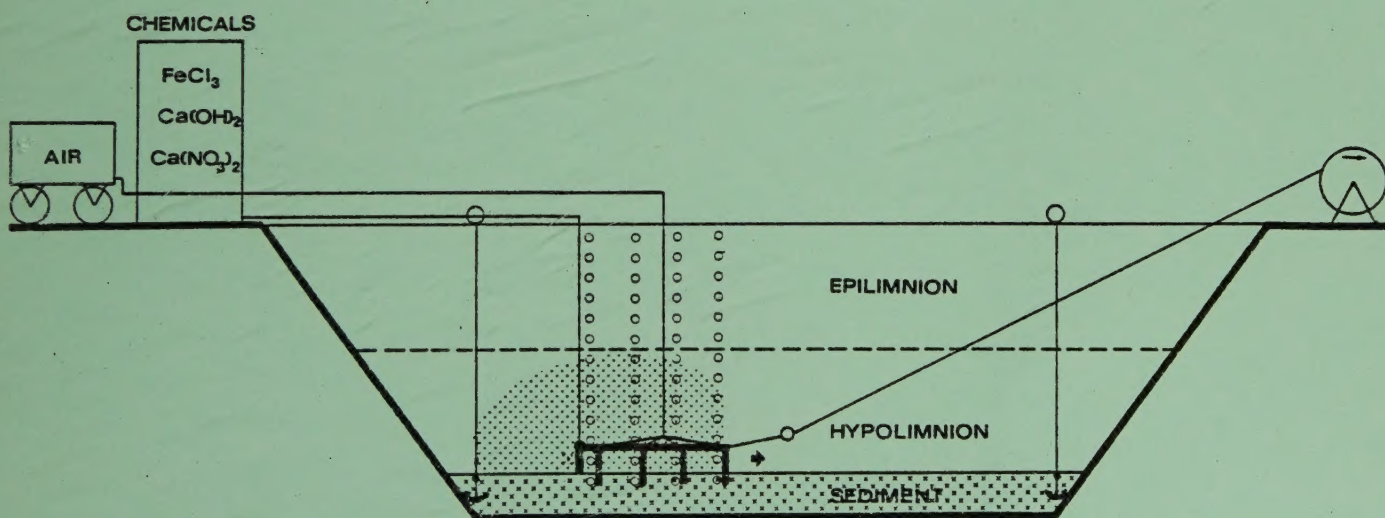


LIMNOLOGISKA INSTITUTIONEN LUNDS UNIVERSITET

OXIDATION OF LAKE SEDIMENTS WITH NITRATE

- A RESTORATION METHOD FOR FORMER RECIPIENTS

Wilhelm Ripl



INSTITUTE OF LIMNOLOGY
University of Lund

LUND 1978

OXIDATION OF LAKE SEDIMENTS WITH NITRATE --
A RESTORATION METHOD FOR FORMER RECIPIENTS

av

Wilhelm Ripl, Mlm

Akademisk avhandling som för avläggande av
filosofie doktorsexamen vid Matematisk-natur-
vetenskapliga fakulteten vid Universitetet i
Lund kommer att offentligen försvaras å Limno-
logiska institutionen, Fabriksgatan 2, Lund,
torsdagen den 1 juni 1978 kl. 10.00.



Lund 1978

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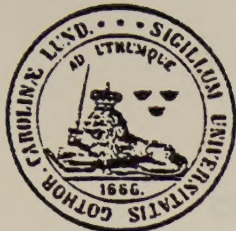
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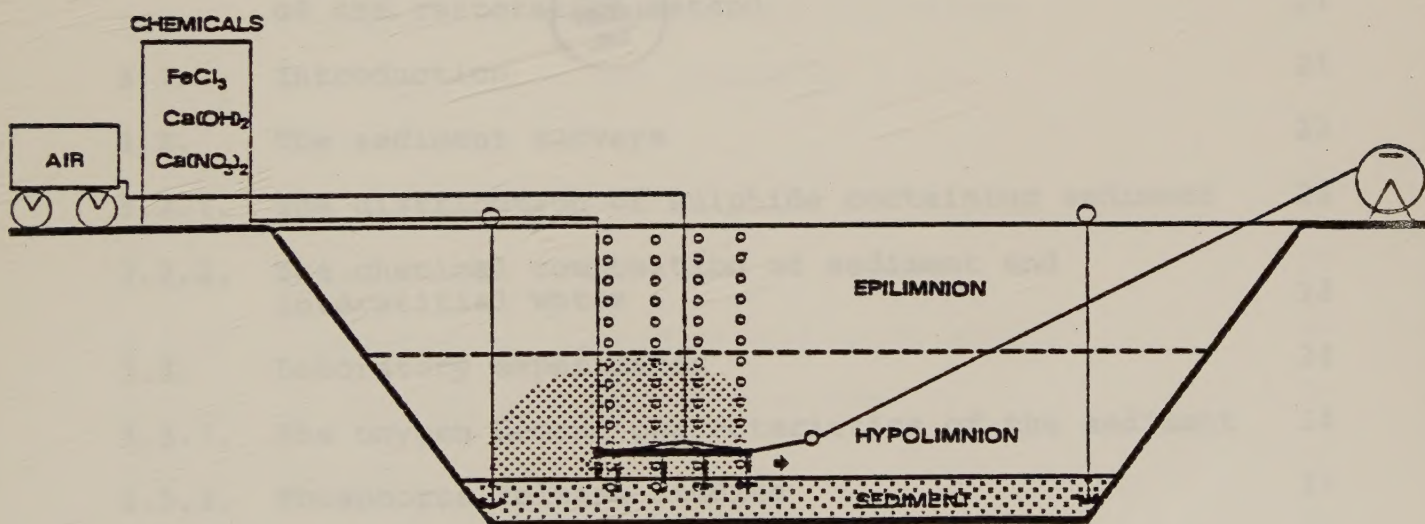


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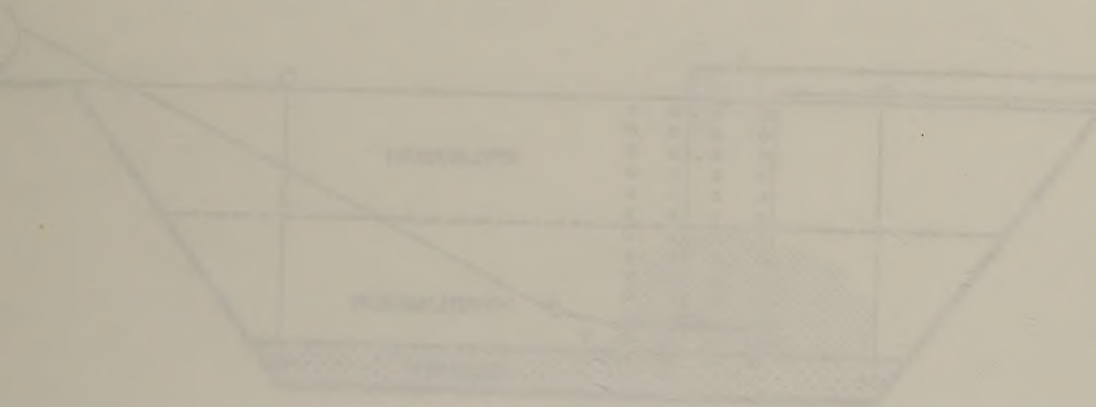
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EXAMINATION OF LIME SEDIMENTS WITH HYDRA
- A REFORMATION METHOD FOR BORON ANALYSIS

1948



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1. Introduction

Eutrophication problems of lakes have long been recognized, and understanding of the relationship between nutrients and planktonic development can be traced back to measures taken in the lake Feuersee close to Stuttgart. Dilution of the lake water with algal-free water was proposed and executed. The method failed, probably due to the poor quality of the water used for dilution. This method was mentioned by Naumann (1915) as a measure to restore lakes. Naumann also described in the same paper the efforts by Kolkwitz to restore Lietzensee in Berlin. In this case dilution with water of good quality was successful. The scientists of these times not only improved conditions in the lake, but with the experience from this project they formulated the first paradigms of production biology for phytoplankton production and biomass development. This quotation by Naumann (op. cit.) stresses the intimate connection between applied and theoretical limnology and the fertility of ideas and experiences gained in the application of restoration methods. Study of the response of various structural components to the restoration measures has, in particular, contributed to enormous gains in both understanding and controlling aquatic ecosystems.

As is well known urbanization and the invention of the water closet had a disastrous impact on most of the lakes in central Europe in and near densely populated areas. Various methods for restoration of polluted lakes have been developed since the dilution of the Lietzensee.

Methods were developed together with sewage treatment technology not

as competitive alternatives but rather as complements and refinements when diversion of sewage showed not to be sufficient for the rehabilitation of the lake ecosystem. The definition of lake restoration in this paper is according to Björk (1968) and thus refers to measures applied directly in the lake with effective sewage treatment measures or diversion as prerequisites.

A large variety of different restoration methods has been developed, and a rather exhaustive review is given by Dunst et al. (1974). Further reviews on the subject with special reference to European lake restoration activities are given by Björk (1974) and Pechlaner (1976).

Three main groups of methods can be distinguished: Mechanical, biological and chemical. Due to the complex structure of aquatic ecosystems with highly interrelated control mechanisms, similar results can be achieved by different methods. On the other hand, no standardized restoration methods which always guarantee successful results exist.

1) Mechanical restoration methods: The cutting of reeds and other aquatic weeds including the extraction of root felts are examples of mechanical methods. Many eutrophicated lakes suffer from excessive macrophyte vegetation, and mechanical vegetation control measures are used in connection with other methods. The removal of sludge deposited during the recipient period of a lake or as a result of erosion can also be considered a mechanical restoration method (Björk 1966, 1972 a, Andersson et al. 1975, Bengtsson et al. 1975).

2) Biological methods: Changes in the ecosystem structure, mainly with respect to fish, have been shown to have a strong influence on the whole ecosystem (Andersson et al. 1978). For the control of aquatic macrophytes grass carp (Ctenopharyndogon idellus) has been used (Liepolt & Weber 1971).

3) Chemical methods: Chemical precipitation of phosphorus has been proposed with a variety of chemical agents such as iron chloride (Pechlaner & Schulz 1973), aluminium sulphate (Landner 1970, Peterson et al. 1973, Barroin 1976) and zirconium compounds (Peterson et al. 1976, Powers et al. 1975). All aeration methods can be grouped with chemical methods. Aeration makes use of the fact that iron compounds usually responsible for the sorption of phosphorus in the sediments show large differences in solubility depending on the redox potential. Anoxic basins are often rich in orthophosphate and iron whereas oxygenated waters loose phosphorus sorbed to trivalent iron compounds (Bengtsson et al. 1972). These methods were used in various lakes in Europe and USA (Mercier 1949, Bernhardt & Hötter 1967, Fast 1971, Bengtsson et al. op. cit., Seppänen 1973). Diversion of hypolimnetic water rich in nutrients was proposed and applied by Olszewsky (1961), and Pechlaner (1971). With aeration methods good oxygen conditions were obtained after short time treatment in the hypolimnion, but oxidation of the lake sediments proved to be difficult. The oxidized layers obtained were only some mm in thickness and were immediately reduced when aeration was terminated in recipients highly loaded with organic matter.

The lake restoration method presented in this study is closely related to the aeration methods, although the oxygen needed for the

oxidation of the superficial sediment layers is contributed by the chemical compound nitrate. The reaction pathways are partially biochemically mediated, but the effects on the sediments are an oxidation of organic matter and an oxidation of reduced inorganic species such as Fe^{++} compounds and S^- compounds. The phosphorus sorbing properties in an oxidized environment are used to inactivate phosphorus and retard internal P cycling (Golterman 1976). The full scale field experiment was carried out in Lake Lillesjön close to the city of Värnamo, central south Sweden.

The work is separated into three parts:

- 1) Sediment surveys, laboratory studies and experiments in connection with the development of the method.
- 2) Development of the field restoration equipment. Restoration and monitoring the results during the denitrification phase.
- 3) Development and change of the lake ecosystem due to the restoration measures.

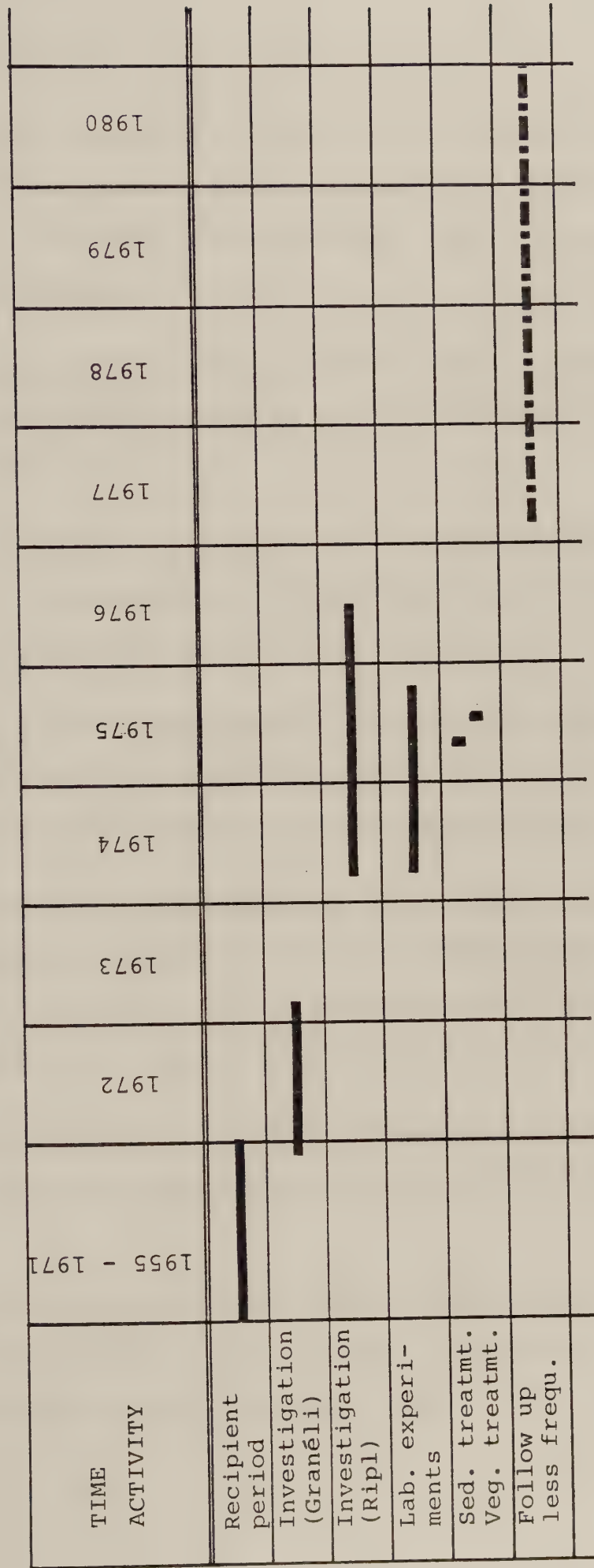
These three parts are compiled in a time-activity diagram (Tab 1) to indicate the time required for development and application of the method and for monitoring studies of the effects.

1.1. Acknowledgements

The author is indebted to Professor Sven Björk for all discussions and suggestions in the field of lake ecosystem control and management, for providing facilities and for reading the manuscript. Docent Anders Södergren is thanked for valuable comments on this paper.

The work could not have been successfully performed without the

Table 1) Time activity diagram.



cooperation of the community authorities in Värnamo, especially town gardener Ulf Helgesson and the Atlas Copco Central Laboratory for Physics with Civ Ing Gunnar Wijk, Ing Jan Petersson and Ing Ingmar Berglund.

The new apparatus for interstitial water sampling was developed together with- and manufactured by Mr Alf Lundberg, glassblower at the University, Lund.

The surveys of organism communities were permormed by FK Amelie Fritzon (phyto- & zooplankton), FK Sven Karlberg (zoobenthos) and FK Olof Lessmark & FK Lars Collvin (fish).

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2. Methods

2.1. Field methods

Water samples were taken with a 2.5 l Ruttner sampler equipped with a mercury thermometer (0-30 °C, d=0.1) calibrated in °C.

Samples for oxygen analysis were taken in 110 ml bottles with conical screw caps, and oxygen was immediately precipitated with MnCl_2 solution and NaOH solution with NaN_3 added.

Polyethene bottles were filled for subsequent analysis of pH, alkalinity, Na, K, Ca, Mg, Cl, SO_4 , Fe, Mn, Cu, Zn and SiO_2 . Borosilicate glass bottles with a volume of 250 ml and glass stoppers were used for samples for nutrient analysis. These samples were preserved with 0.5 ml of 4 % HgCl_2 solution.

For the quantitative study of phytoplankton, 110 ml of the water samples were preserved with Lugol's solution. For the qualitative study of phytoplankton and zooplankton, net samples were taken with a 10 μm mesh-size net. The samples were preserved with concentrated formalin solution to 4 %.

Transparency was usually measured with a white Secchi disc with a diameter of 150 mm without optical aids.

Sediment samples were taken with a Kajak-type tube corer (Berggren 1972) in perspex tubes with an inner diameter of 69 mm and an outer diameter of 75 mm. The length of the tubes was 515 mm and the sediment cores taken had a height of 250-300 mm. During the vegetation period (May to September) pH was measured immediately on the shore.

The samples were transported immediately to the laboratory and pretreated for the different analyses.

2.2. Laboratory methods

Water was filtered by vacuum filtration with an aspirator for the analysis of dissolved compounds. Whatman GF/C filters were used for nutrients (phosphorus and nitrogen fractions), and Munktell V100 acid-treated paper filters were used for the analysis of various ionic components (macro constituents) and silica.

Sediment cores were sliced and the dry weight determined after drying over night (12-20 h) at 105 °C. Loss on ignition was determined after ignition in a muffle-furnace at 550 °C.

Part of dry matter was digested with a mixture of concentrated perchloric acid and nitric acid 1:4 for subsequent analysis of various metals and phosphorus. The acid-insoluble residue was filtered through a Munktell 00 ashfree filter and was weighed after ignition at 550 °C. Another portion of the dry matter was weighed for Kjeldahl digestion.

Interstitial water was sampled in two different ways:

- 1) Sediment was filtered in a Sartorius pressure filtration device through a Sartorius 0.45 µm filter under nitrogen (0.2-0.6 MPa). The interstitial water samples were subsequently analyzed for $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, Fe, Mn, $(\text{NO}_3+\text{NO}_2)\text{-N}$, conductivity, pH and alkalinity.
- 2) For the monitoring of the restoration measures a dialysis sampling technique was developed. This method is described

in detail at the end of this chapter and proved to be superior to pressure filtration for interstitial water.

2.3. Chemical and physical water and sediment analyses

pH of the water samples was determined electrometrically with a combined glass-calomel electrode after calibration of the instrument with 2 buffers to a precision of ± 0.02 pH units.

Alkalinity was titrated acidimetrically with 0.01 N HCl in a nitrogen-flushed chamber to a final pH of 5.4. The different components of the carbonic acid system and the total inorganic carbon fraction were computed using the apparent equilibrium constants given by Buch (1945). These constants were interpolated for ionic strength and temperature.

Oxygen and H_2S were determined iodometrically. H_2S in the sediment was transferred from the acidified sediment to a solution of CdSO_4 with N_2 gas and precipitated as CdS. Oxygen saturation values were calculated by interpolation of the saturation values given by Mortimer (1956).

The oxygen demand in the sediment was determined by two different methods:

- 1) In a Voith Sapromat at 20 °C under stirred conditions. This method was used to study the effects of sediment oxidation with nitrate.
- 2) According to the method developed by Granéli on "undisturbed" sediment cores incubated at the in situ temperature, (Granéli 1977 a). This method was used to monitor the oxygen demand in

the restored lake.

Water colour was measured colorimetrically (Hellige Aqua Tester) using coloured glass discs as artificial Pt standards.

Turbidity was determined in a Hach Turbidimeter and was standardized by an artificial glass standard in JTU (Jackson Turbidity Units).

Na, K, Ca, Mg, Fe, Mn, Cu and Zn were determined by atomic absorption spectroscopy on a Perkin Elmer 303 according to the standard procedures given by Perkin Elmer. La-Al buffer was added to samples analyzed for Ca and Mg, and Cs ions were added to samples analyzed for Na and K.

Cl was determined argentimetrically with an electrometric end point indication (AgCl-HgSO_4 electrodes in sulfuric acid environment).

SO_4 was determined indirectly by quantitative cation exchange on a Dowex 50WX8 50-100 mesh H^+ -charged ionic exchange resin and acidimetric determination of the sum $\text{NO}_3^- + \text{Cl}^- + \text{SO}_4^{=}$.

All nutrient fractions (P, N, SiO_2) were analyzed colorimetrically on a Technicon Auto Analyzer II. Tot-P was determined (in water samples) after digestion in an autoclave with K-persulphate as oxidant and in sediment samples after digestion with a mixture of nitric- and perchloric acid (4:1). The liberated orthophosphate was transformed to the molybdenum blue complex by reducing the phosphoheteropolymolybdate complex with ascorbic acid at 70°C . The mercury added for preservation of the sample was masked by

cystein. Kjeldahl nitrogen was determined after digestion of the samples in concentrated H_2SO_4 at a temperature of 380°C (K_2SO_4 addition) with Cu as catalyst. $\text{NH}_4\text{-N}$ was then reacted without distillation to the indophenolic blue complex by a Berthelot reaction. $\text{NO}_3\text{-N}$ was determined after a reduction to $\text{NO}_2\text{-N}$ in a copperized reductor and diazotation by a Griess reaction. Silica was determined by reducing a silicoheteropolymolybdate complex to the molybdenum blue complex with ascorbic acid.

2.4. Qualitative and quantitative determination of plankton

Formalin fixed net samples and original water samples fixed with Lugol's solution were used for the qualitative analysis of phytoplankton. Quantitative determination was done by counting cells in an inverted microscope according to Utermöhl (1958). For common species at least 100 cells distributed over at least 2 different diagonal fields were counted; for less frequent organisms the whole area of the counting chamber was used. Counting chambers with volumes of 0.16, 2.2, 5, 10 and 25 ml were used.

For the estimation of organism volumes 10 species were measured on each sampling occasion. The formulae used to approximate volume were according to Willén (1976).

For the zooplankton survey netplankton samples were examined and the abundance of the organisms present estimated as:

+ = single specimens found, ++ abundant and +++ frequent.

2.5. Estimation of the relative biomass of fish

Fish surveys were conducted on two occasions with survey links. This net type consists of combined links with mesh widths of 9.5, 14.5, 18, 24, 29.5, 33, 38 and 46 mm. The link is 56 m long and 1.5 m wide. These nets were placed at various depths to obtain representative samples for the entire lake. Numbers of fish in the different length classes caught were corrected for the selectivity of the different mesh widths of the nets (Hamrin 1975). The relative biomasses obtained are useful in comparison but are not actual biomasses in kg. The ages of the fish were determined by analysis of scales (Kempe 1962).

2.6. Bottom fauna (zoobenthos)

Bottom fauna was collected on two occasions. The sediment was sampled with an Ekman dredge with a sampling area of 225 cm^2 or with a Kajak-type tube corer (Berggren 1972) using perspex tubes with an area of 95 cm^2 . The Ekman dredge was only used at the 2 m sampling site before restoration because of difficulty in penetrating the submerged vegetation. At least four independent samples were taken at each sampling site. The samples were sieved in the field through a 0.55 mm mesh and fixed with formalin to a final concentration of 4 %.

2.7. Laboratory experiments

Sediment cores were incubated with different chemical additions at both room temperature and at $4-6^\circ \text{C}$ in the dark. The sediment

cores were kept in the original perspex tubes, and the water above the sediment was partially replaced by nitrate, iron and Ca(OH)_2 solutions. The laboratory systems were sealed with specially designed polyethene stoppers with a gas-collecting funnel, a magnetic stirrer and glass tubing for sampling the solutions above the sediment. The gas developed in the systems was collected, measured and analyzed for O_2 , N_2 , CO_2 and CH_4 (Fig 1).

Gas analysis was performed on a Varian 1520 gas chromatograph equipped with two columns in series. The columns were made of PTFE tubing and filled with:

- a) Porapak Q 80 - 100 mesh, 4.5 mm x 4.05 m, for the separation of CO_2 and methane.
- b) A mixture of molecular sieves 15 % 5A and 85 % 13X 30 - 60 mesh, 3.0 mm x 5.05 m, for the separation of N_2 and O_2 .

Both columns were operated at 22 °C with a He flow of 50 ml/min. Thermal conductivity detectors operated at 170 mA were used for the detection of the gases. A typical chromatogram is shown in Fig 2.

2.8. Sampling interstitial water in sediment cores and in situ with a new dialysis technique

Automation of chemical analyses allows a drastic reduction of sample volume and enables new sampling techniques. The pore water (= interstitial water) of lake sediments has been analyzed for various ionic species in order to trace parameters required for the description of dynamic aspects of sediment metabolism. Various methods of obtaining interstitial water have been proposed by, for

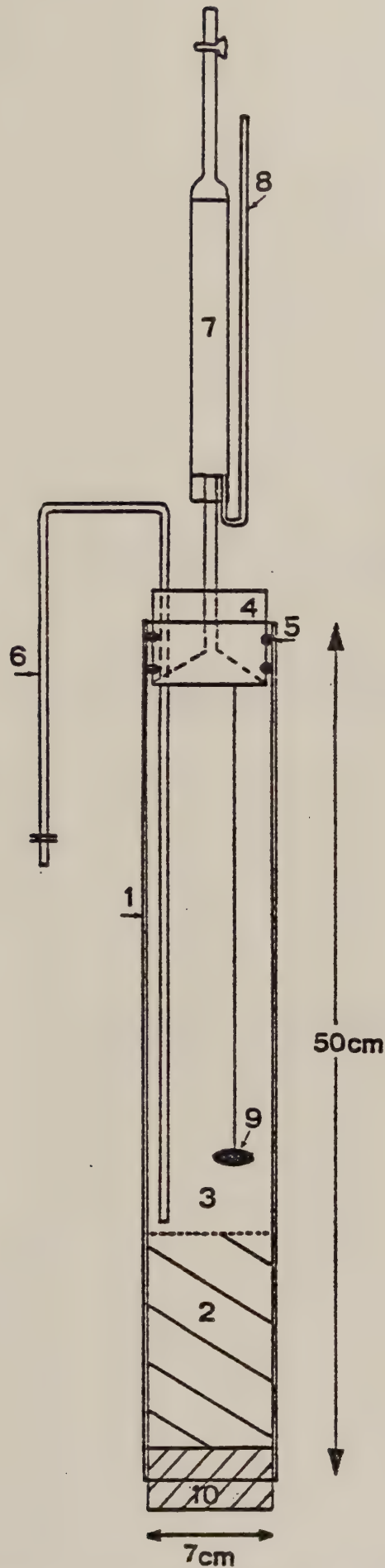


Fig 1) Apparatus used for denitrification experiments: 1) perspex tube, 2) sediment, 3) water above sediment, 4) PVC stopper with funnel for gas collection, 5) O-ring, 6) tube for removal of water samples, 7) cylinder for collecting and measuring gas, 8) open overflow, 9) magnetic stirrer operated by external magnet, 10) rubber stopper.

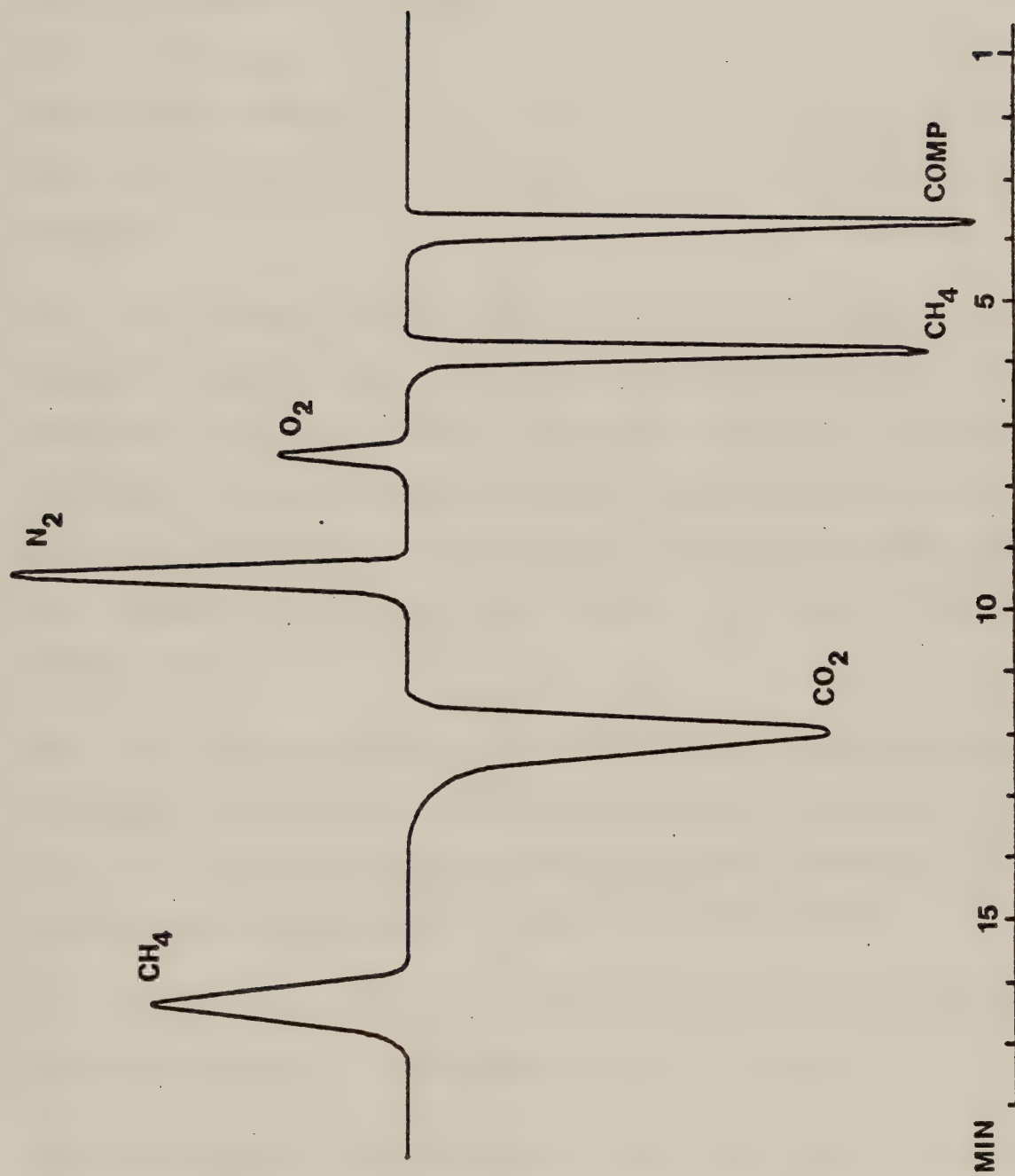


Fig 2) Example of gas chromatogram of gas mixture. Injected volume 0.5 ml, TC-detector current 170 mA, carrier gas He, 0.4 MPa, 50 ml/min, attenuation 32X. Peak denoted COMP is unresolved composition peak for the gases $\text{O}_2 + \text{N}_2$.

example Barnes (1973), Fanning & Pilson (1971), Rudd & Hamilton (1975), Mayer (1976) and Hesslein (1976).

The method described here differs from previous methods by the use of a simple borosilicate glass apparatus covered with tight fitting dialysis tubing (Fig 3). The geometry of the device creates favourable conditions with respect to equilibration time, subduction effect and efficiency compared to filtration with nitrogen pressure.

The ratio between concentrations of various chemical species obtained by the dialysis tube technique and filtration in different sediments is given in Fig 4. The equilibration of the enclosed solution (initially distilled water) with the outer environment after an incubation of 48 hours was over 85 % of that obtained at incubations of 96 hours and longer at all solute concentrations (Fig 5).

The long incubation times (96 hours) led in some cases with biologically highly active sediments incubated at 25 °C to degradation and / or interaction with the dialysis membrane. Incubation times were therefore kept between 48 and 72 hours.

The influence of temperature on the equilibration time of $\text{NH}_4\text{-N}$ is shown in Fig 5 for temperatures 4 °C and 23 °C.

Tubes incubated in solutions of known concentration required shorter equilibration times than tubes inserted in sediment. This effect is probably due to biologically degradation activities, changes in sediment structure and ionic exchange properties with the

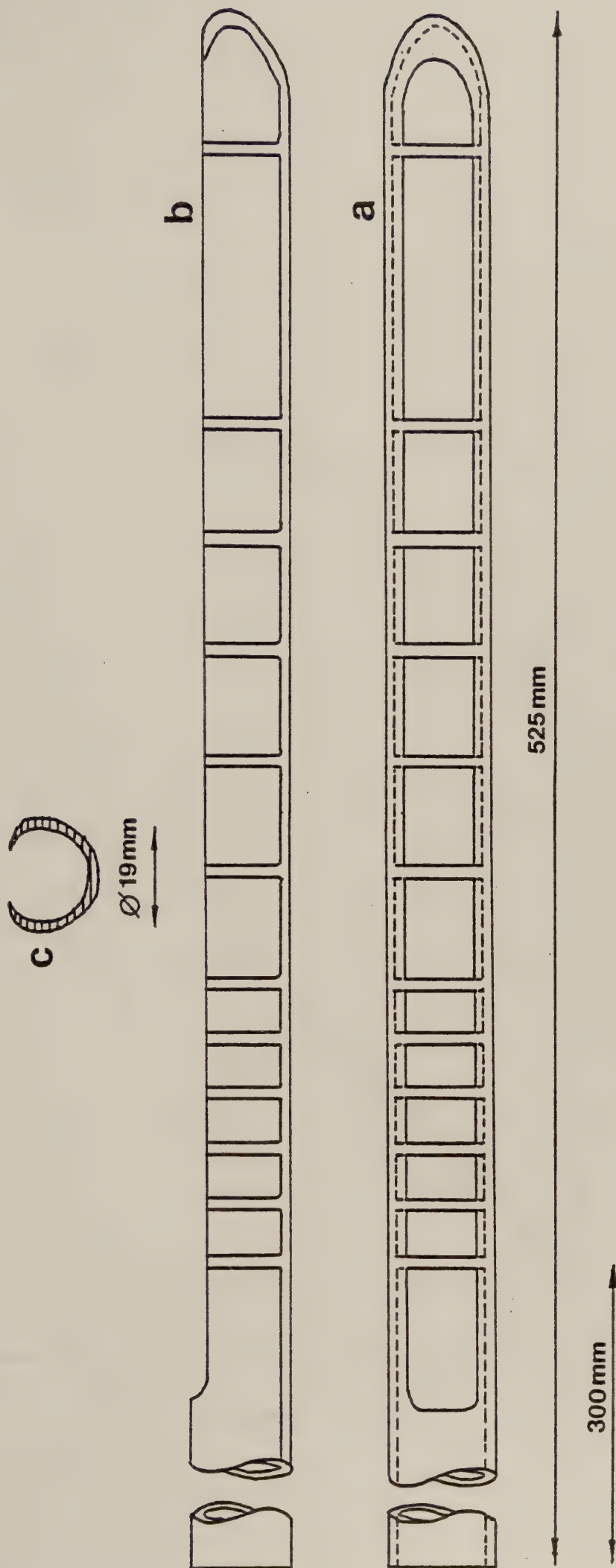


Fig 3) Segmented glass channel used for sampling interstitial water by dialysis a) Front, b) Side
 c) Cross section (the apparatus was manufactured by the glassblower Alf Lundberg, University of Lund).

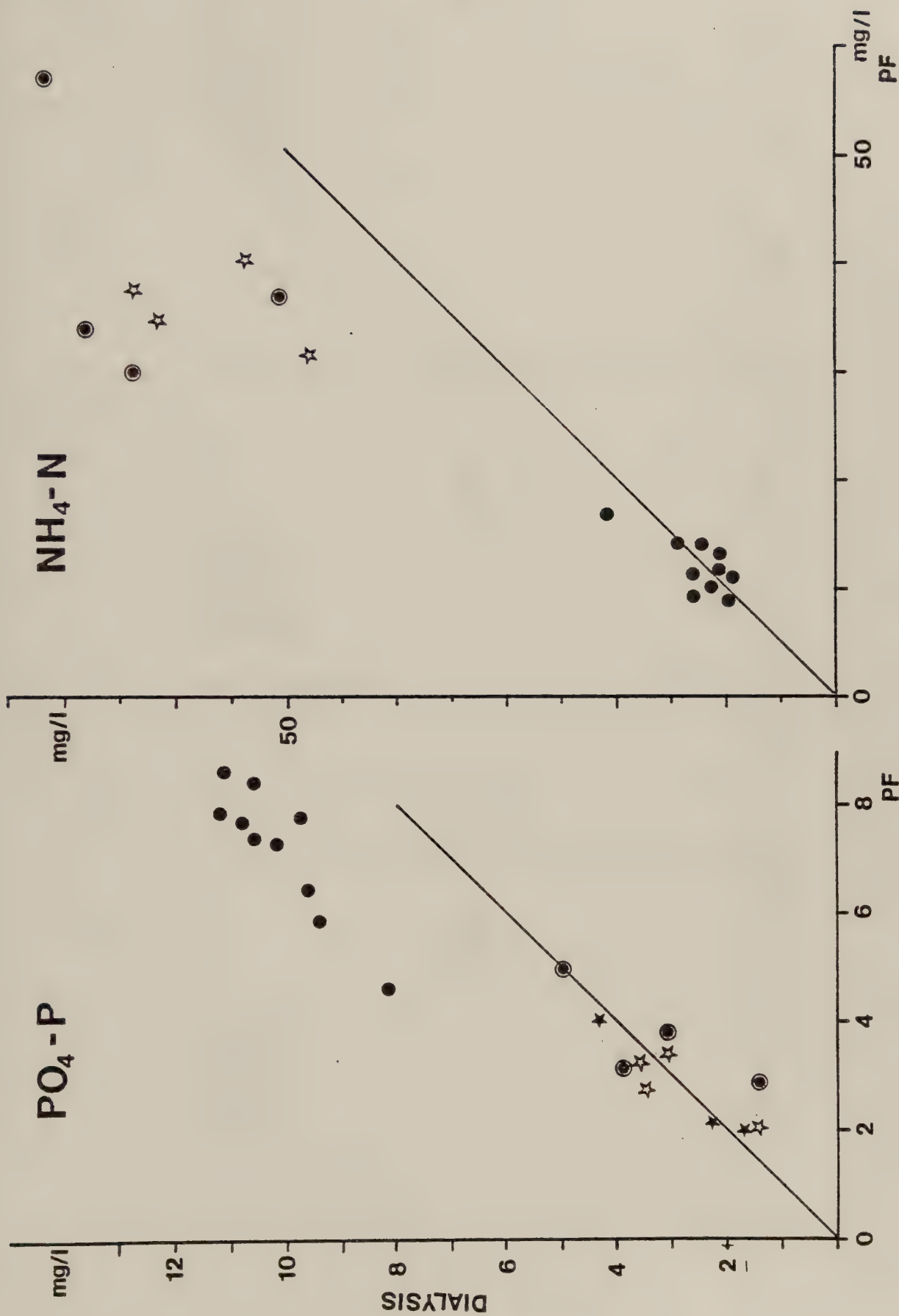


Fig 4) Concentrations of PO_4-P and NH_4-N in interstitial water obtained by pressure filtration (PF) (x-axis) and the dialysis method (y-axis) for various gyttja sediments. The four symbols designate four different sediments.

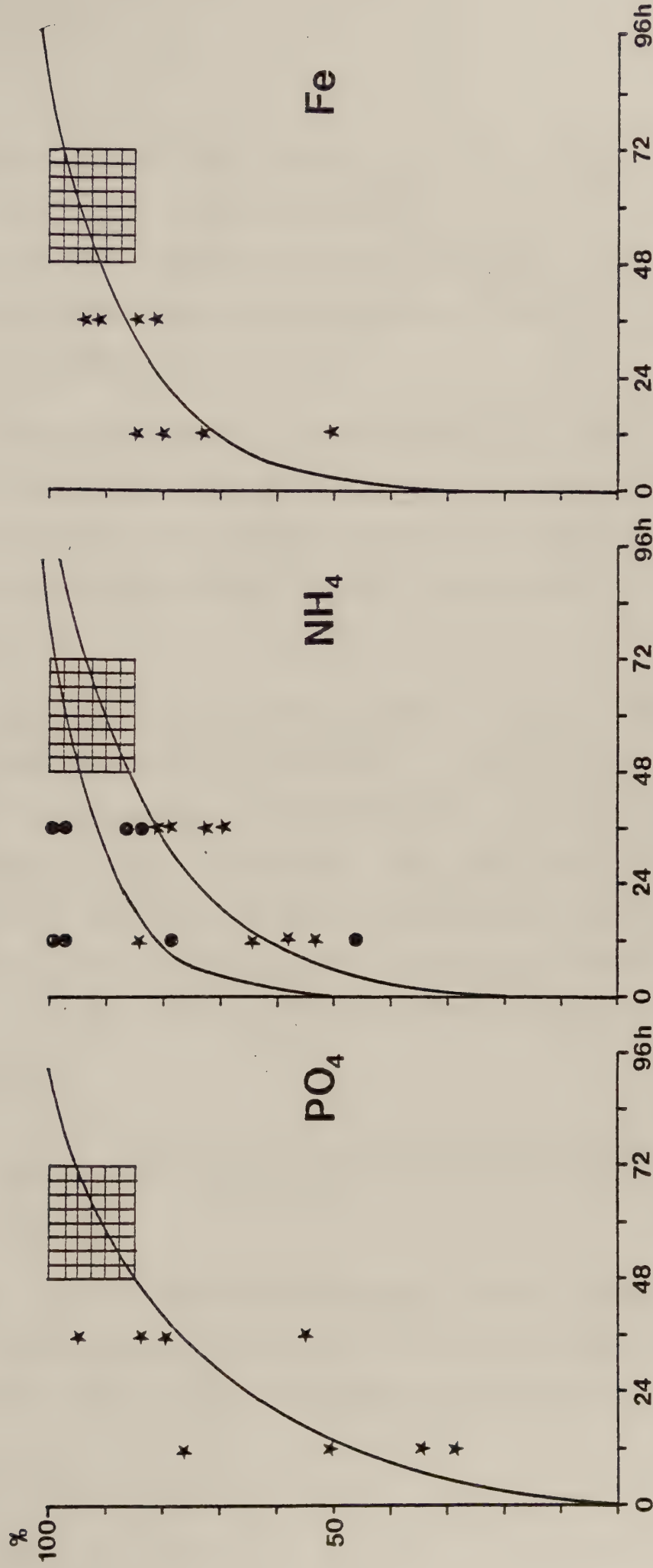


Fig 5) Concentrations of PO₄, NH₄ and Fe in the dialysis sampler (Fig 3) as % of the concentrations achieved after 96 h incubation at 5 °C (●). For NH₄, even incubation at 25 °C (★). The marked areas denote the equilibration times used in the experiments.

diffusion process. The curves in Fig 5 a, b and c were for this reason fitted as simple logarithmic functions since the necessary conditions for a more theoretical treatment by e. g. Ficks law of diffusion were lacking (no temperature-dependent diffusion constant could be estimated).

The effects of subduction (intermixing of sediment strata upon insertion of the tubes were evaluated by inserting the tubes and moving them in a horizontal plane. No significant differences in the results were obtained between these tubes and tubes simply inserted.

The variability between three different tubes incubated in situ was determined for $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ in the following way: The tubes, with a length of 55 cm divided in 2.5 cm compartments, were incubated in situ for 48 hours. For each level the mean and the % deviation of each tube from the mean was calculated. These % deviations were pooled for all compartments ($n=66$) for $\text{PO}_4\text{-P}$ $\bar{x} = 10.9 \%$, $\bar{s}_x = 9.0$, $s_x^- = 1.11$ and $\text{NH}_4\text{-N}$ $\bar{x} = 9.2 \%$, $\bar{s}_x = 7.3$, $s_x^- = 0.9$.

2.9. Statistical treatment of sediment and interstitial water analyses

To show significance of differences for the various parameters, 95 % confidence intervals are given in the figures whenever possible ($n \leq 4$) for both sediment and interstitial water analyses.

3. Sediment surveys, laboratory studies and experiments in connection with development of the restoration method

3.1. Introduction

Investigation of the following parameters in the field and in laboratory experiments was required during development of the restoration method:

- 1) The distribution and thickness of the sulphide-containing sediment layers in Lake Lillesjön.
- 2) The chemical composition of sediment and interstitial water.
- 3) The oxygen demand characteristics of the sediment and the efficiency of sediment oxidation by denitrification.
- 4) Phosphorus exchange properties of sediment cores incubated with and without nitrate.
- 5) Denitrification properties of the various sediment cores, in order to estimate:
 - a) The amount of nitrate and other chemicals to be added to the sediment.
 - b) The required mixing depth to decrease oxygen demand and phosphorus release in the sediment.
 - c) The time required for the total disappearance of added nitrate.
- 6) The effects of the added chemicals on benthic organisms.

3.2. The sediment surveys

3.2.1. The distribution of sulphide-containing sediment

Below a water depth of 3 m, an area of about 0.8 ha in the central part of Lake Lillesjön was covered by a layer of black, iron sulphide (FeS)-containing sediment (cf. Fig 6). The average thickness of this layer was 12 cm (range 1-15 cm).

3.2.2. The chemical composition of sediment and interstitial water

The chemical composition of sediment dry matter and of the interstitial water was determined on 4 occasions at 3 sampling sites (2, 3 and 4 m water depth, cf. Fig 6). The results indicated significant heterogeneity for several parameters. Temporal variations in chemical composition were therefore difficult to resolve. However, seasonal variations in the sediment interstitial water concentrations of $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, Fe and alkalinity were observed mainly in the upper 5 cm. Concentration gradients in interstitial water are usually affected by temperature and mixing in the water column above the sediment (Ripl & Lundquist 1977).

A comparison between analyses of interstitial water extracted by pressure filtration with nitrogen gas and analyses of samples collected by the dialysis technique revealed that mixing of interstitial water from the upper sediment strata with the water above the sediment occasionally occurs when the cores are taken and transported. Therefore, even for the analyses of interstitial water, mean values before and after restoration for the various

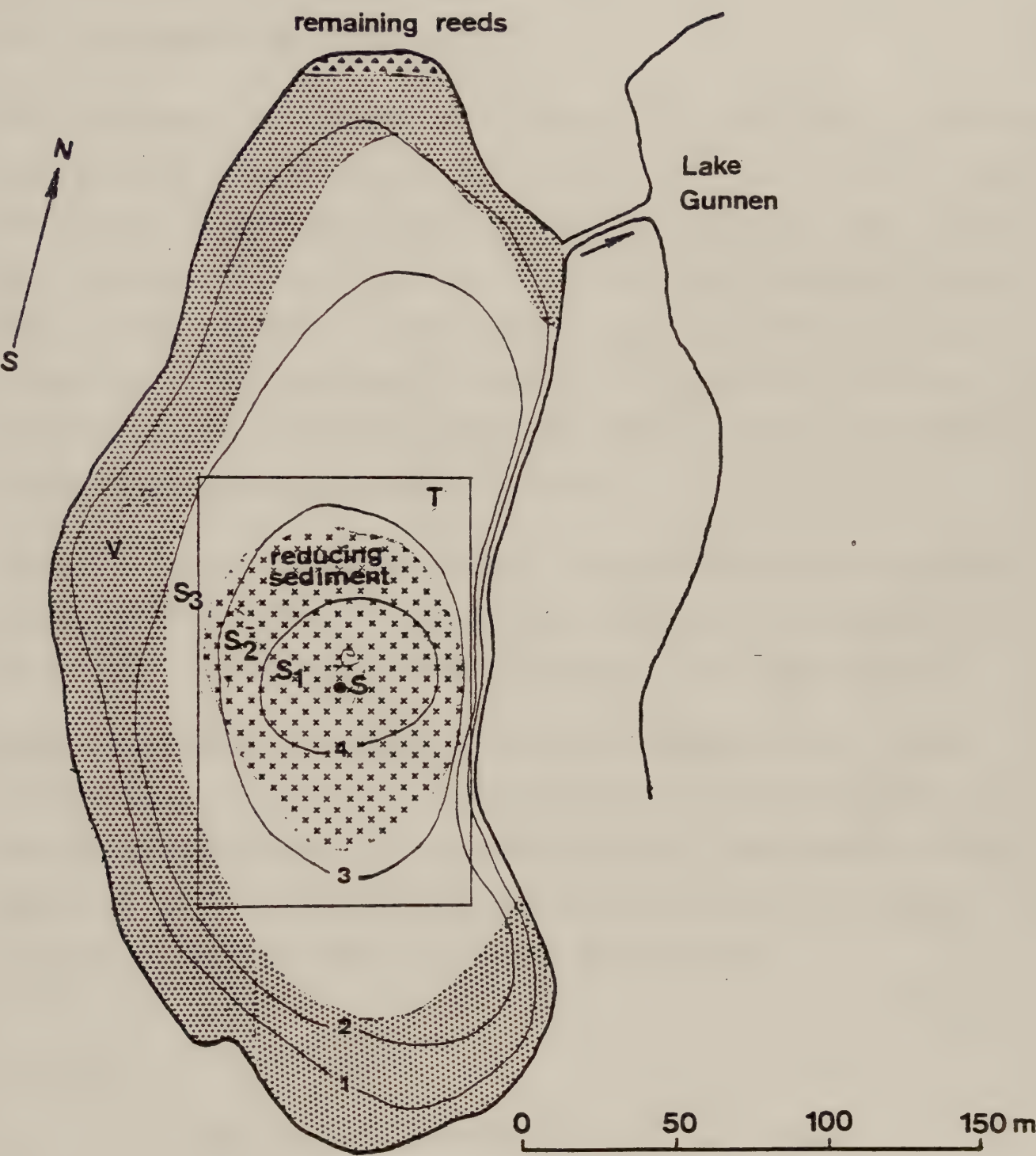


Fig 6) Map of Lake Lillesjön with depth contours, extent of vegetation (V) and extent of sulphide containing sediment. S central sampling station, S₁, S₂ and S₃ sampling sites for sediment. T treated sediment area.

strata were calculated. The amplitude of seasonal variations can be seen by the breadth of 95 % confidence intervals for values from the superficial sediment zones.

The composition of the sediment, disregarding the layers containing iron sulphide, was similar in the cores taken at 2, 3 and 4 m water depth (Fig 7, Fig 8 and Fig 9). Sulphide was obtained only in sediments deposited below 3 m water depth. The concentrations of sulphide in the sediment on a dry matter basis were between 8.6 and 0.6 mg S/g, with the highest values in the upper 5 cm layer and the lowest concentrations in the layer 5-10 cm. Below 10 cm only traces of sulphide were usually detected.

Large differences in distribution of the various nutrient species in interstitial water were found when sediment cores taken at different water depths were compared (Fig 10, Fig 11 and Fig 12).

These differences concerned: 1) absolute concentrations, 2) the vertical distribution of concentrations and 3) the variation amplitude of concentrations. Lower concentrations, orthograde distribution with depth and greater homogeneity were generally observed in sediment samples taken at a water depth of 2 m.

3.3. Laboratory experiments

3.3.1. The oxygen demand characteristics of the sediment

Oxygen demand studies with the "Sapromat" were carried out to compare sediments from different sites and with different treatments. Three phases could be distinguished in the sediment oxida-

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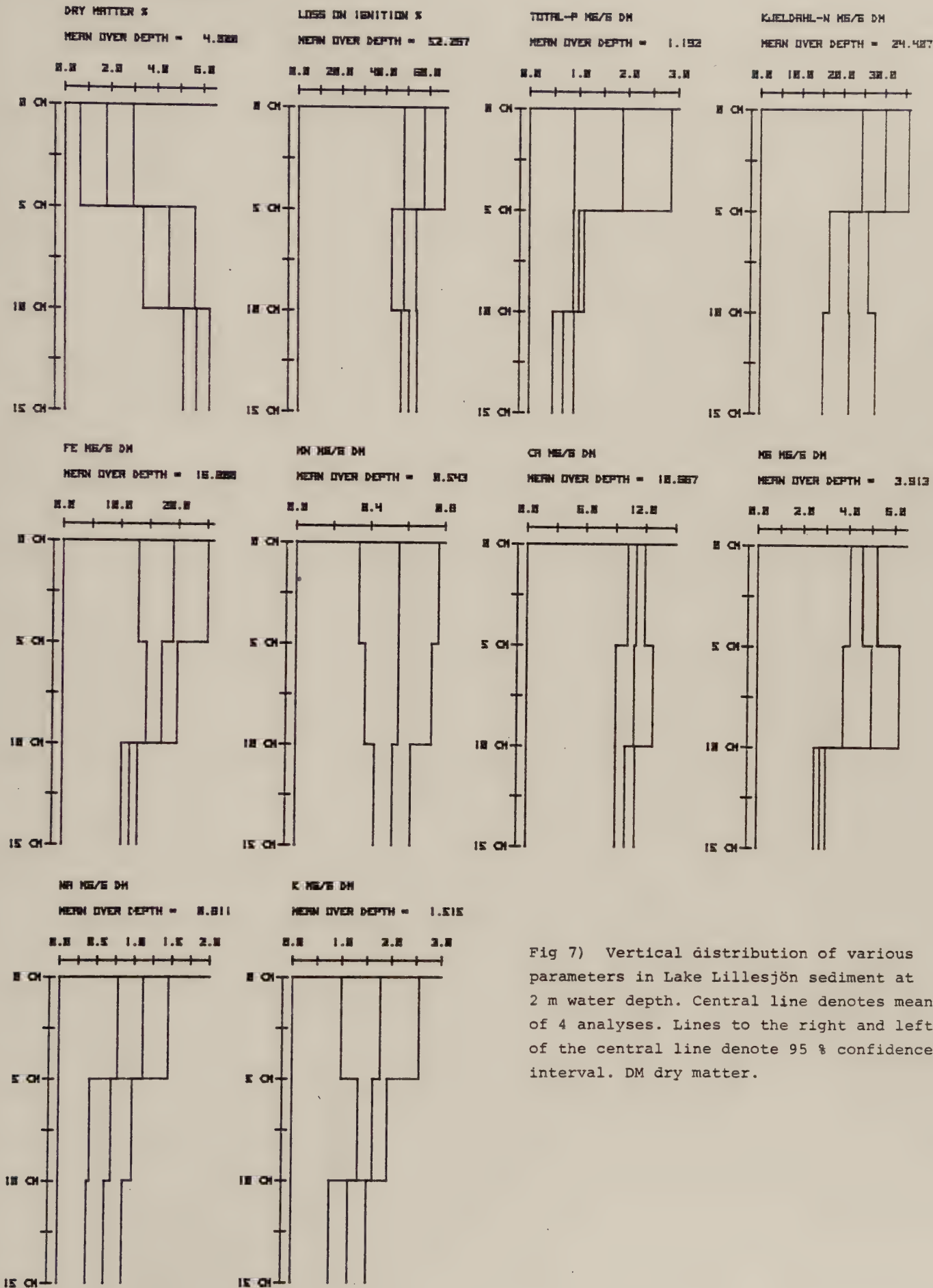


Fig 7) Vertical distribution of various parameters in Lake Lillesjön sediment at 2 m water depth. Central line denotes mean of 4 analyses. Lines to the right and left of the central line denote 95 % confidence interval. DM dry matter.

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DRY MATTER %

MEAN OVER DEPTH = 4.647

LOSS ON IGNITION %

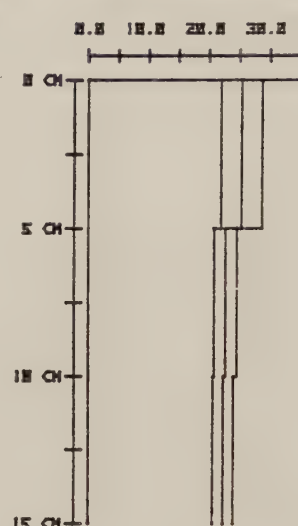
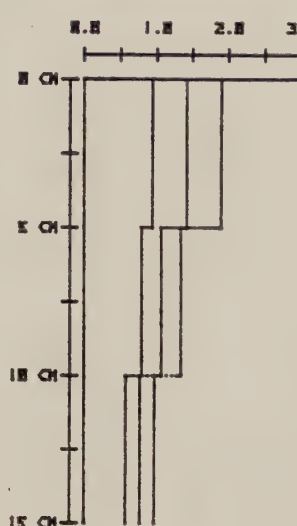
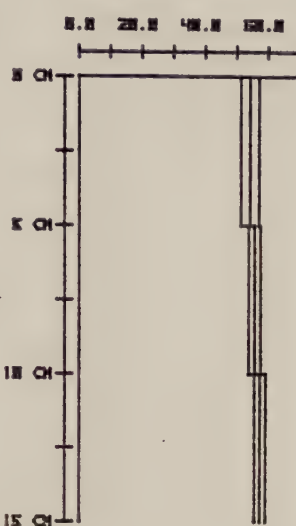
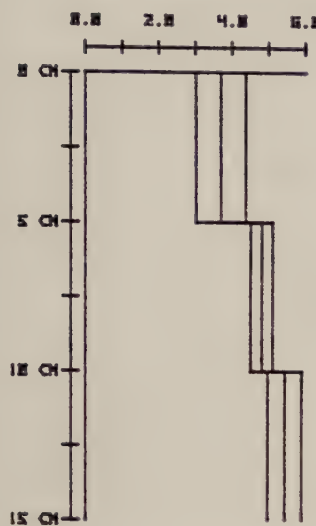
MEAN OVER DEPTH = 55.773

TOTAL-P MG/G DM

MEAN OVER DEPTH = 1.085

KJELDAHL-N MG/G DM

MEAN OVER DEPTH = 23.457



FE MG/G DM

MEAN OVER DEPTH = 18.432

MN MG/G DM

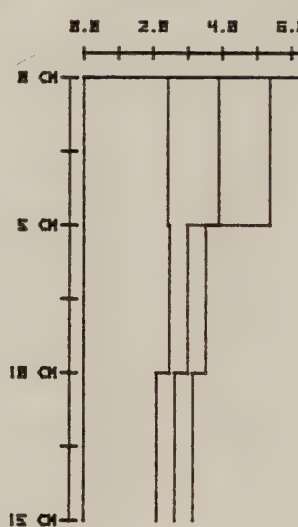
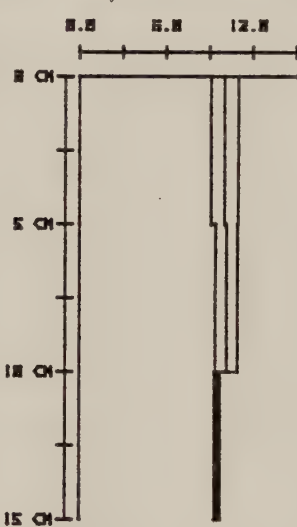
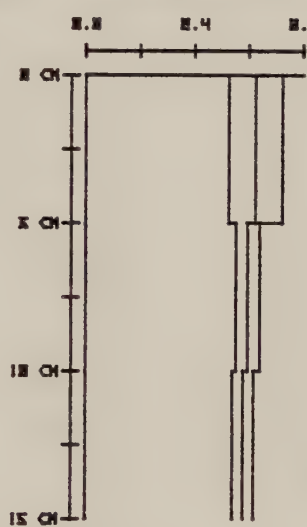
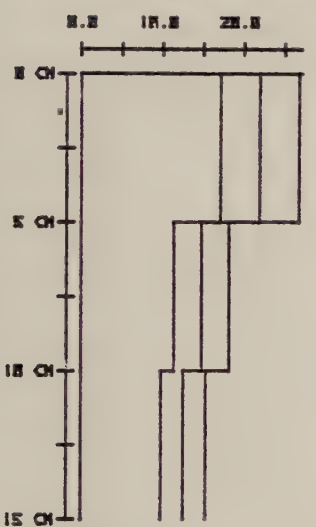
MEAN OVER DEPTH = 8.881

CA MG/G DM

MEAN OVER DEPTH = 8.827

MG MG/G DM

MEAN OVER DEPTH = 3.187



NR MG/G DM

MEAN OVER DEPTH = 8.738

K MG/G DM

MEAN OVER DEPTH = 1.264

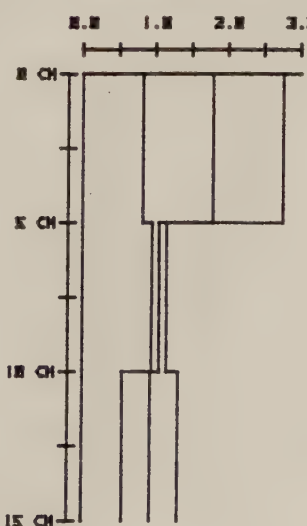
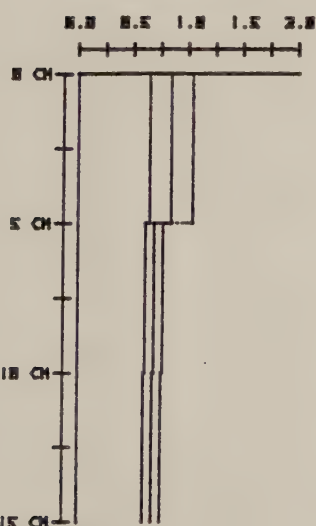


Fig 8) Vertical distribution of various parameters in Lake Lillesjön sediment at 3 m water depth. Central line denotes mean of 4 analyses. Lines to the right and left of the central line denote 95 % confidence interval. DM dry matter.

LAKE LILLESJÖEN

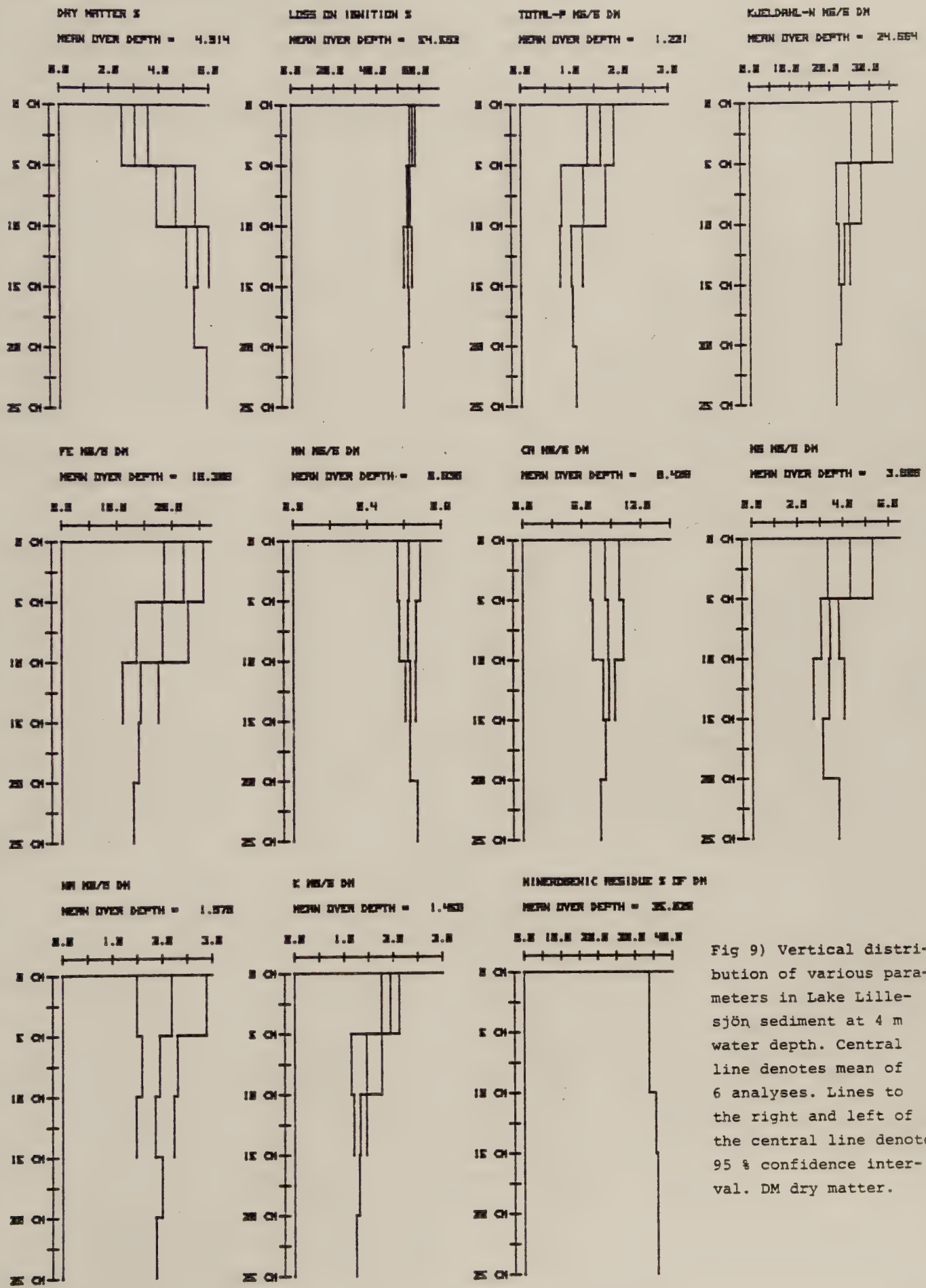


Fig 9) Vertical distribution of various parameters in Lake Lillesjön sediment at 4 m water depth. Central line denotes mean of 6 analyses. Lines to the right and left of the central line denote 95 % confidence interval. DM dry matter.

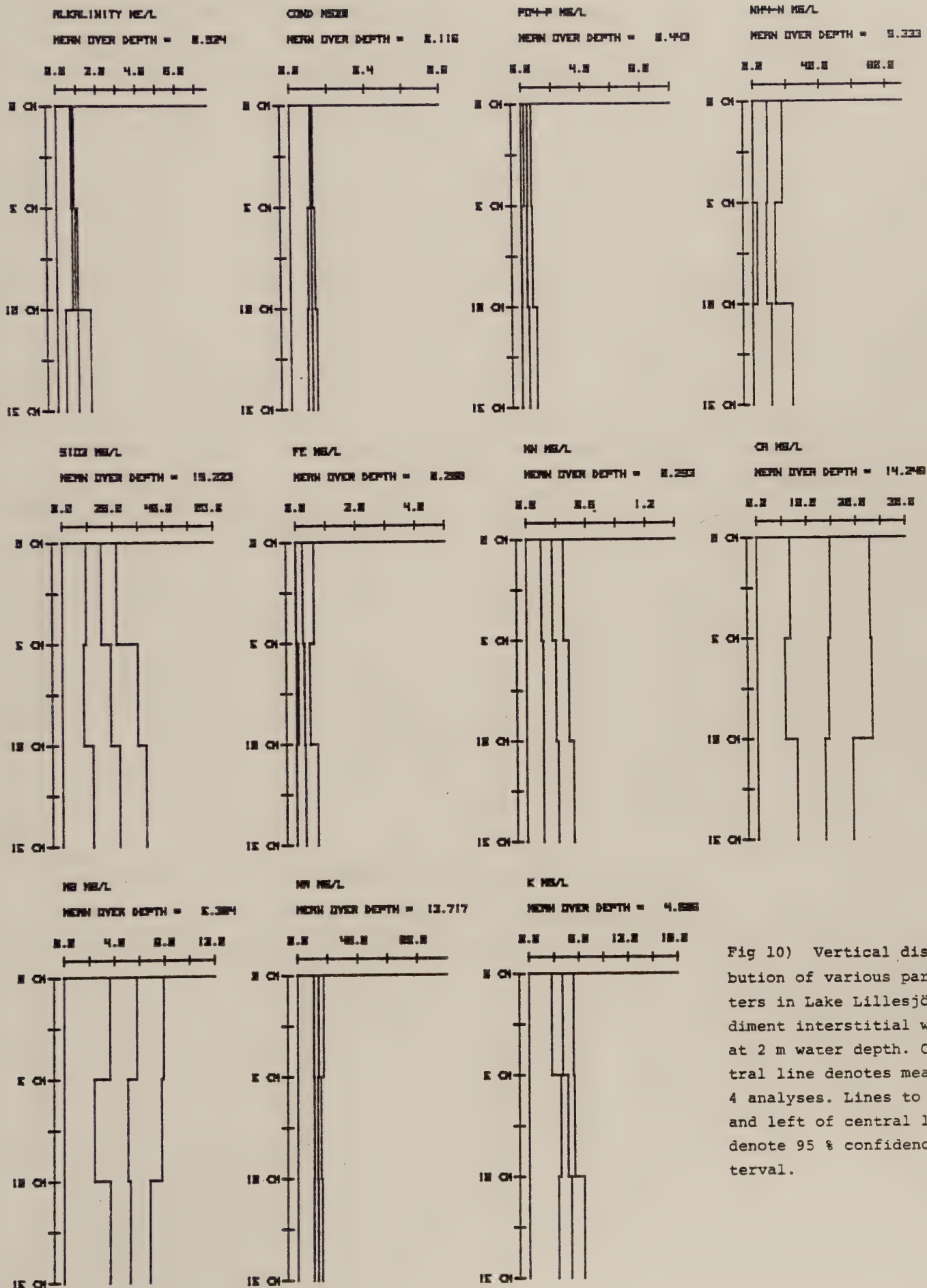


Fig 10) Vertical distribution of various parameters in Lake Lillesjön sediment interstitial water at 2 m water depth. Central line denotes mean of 4 analyses. Lines to right and left of central line denote 95 % confidence interval.

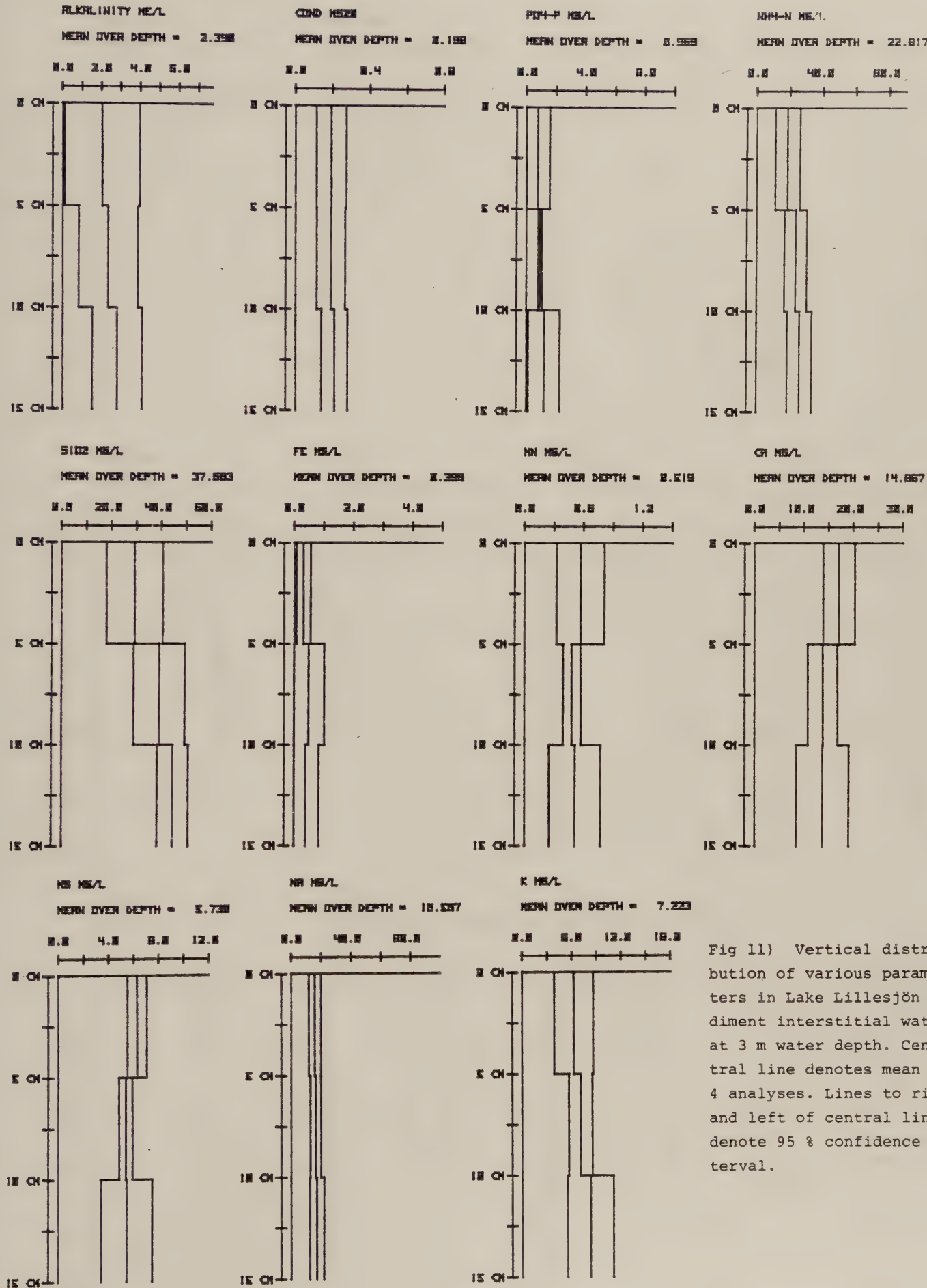


Fig 11) Vertical distribution of various parameters in Lake Lillesjön sediment interstitial water at 3 m water depth. Central line denotes mean of 4 analyses. Lines to right and left of central line denote 95 % confidence interval.

LAKE LILLESJÖN

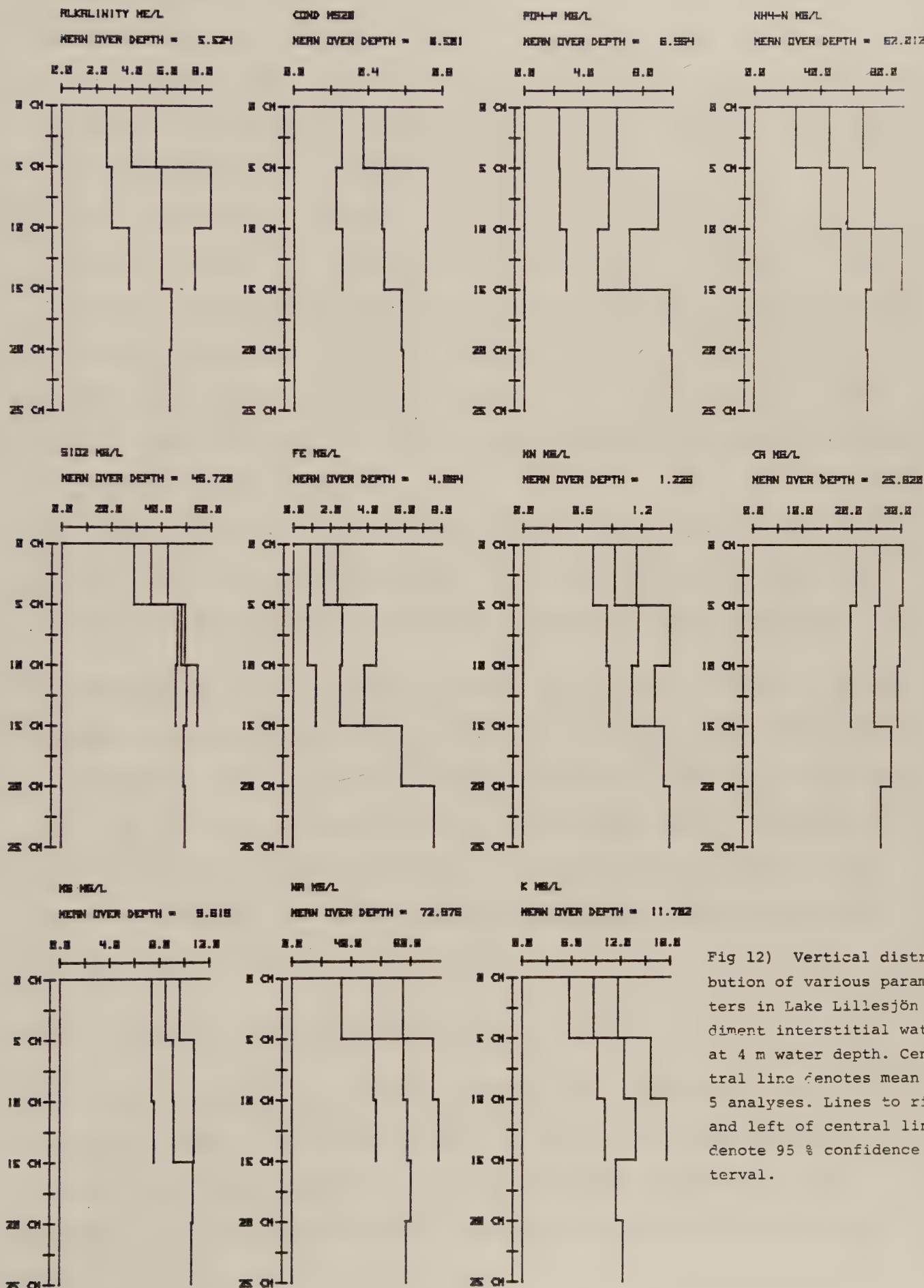


Fig 12) Vertical distribution of various parameters in Lake Lillesjön sediment interstitial water at 4 m water depth. Central line denotes mean of 5 analyses. Lines to right and left of central line denote 95 % confidence interval.

tion process:

- 1) The initial phase, with a rapid oxidation of inorganic compounds. FeS , Fe^{++} and H_2S are readily oxidized and cause the initially steep slopes of the oxygen uptake curves.
- 2) The second phase (between the 2nd and 10th day), with the oxidation of ammonia by nitrifying bacteria and the oxidation of easily degradable organic matter (dissolved organic matter and certain side chains coupled to particulate organic matter).
- 3) The third phase, characterized by almost linear oxygen uptake with time. This is the oxidation of particulate organic matter by attached bacteria.

The oxygen uptake of NO_3 -treated sediment samples and untreated sediment from various depths and sites was used to evaluate the effects and efficiency of sediment treatments (Fig 13 and Fig 14).

An extrapolation of the more or less linear part (phase 3) of the oxygen consumption (Sapromat) curve back to the y-axis indicates an immediate (phase 1 and 2) oxygen demand of 3-4 g O_2 /l sediment (cf. Fig 14). The sediment at 3 m water depth showed transitional properties between the sediments at 4 and 2 m water depth, contained relatively low interstitial ion concentrations and showed low initial oxygen demand.

3.3.2. Phosphorus release studies

Most of the phosphorus release studies were performed with the sediment cores in the dark at 4-6 °C under anaerobic conditions. Results from experiments at room temperature proved to be unreliable in some cases due to large gas production and were omitted.

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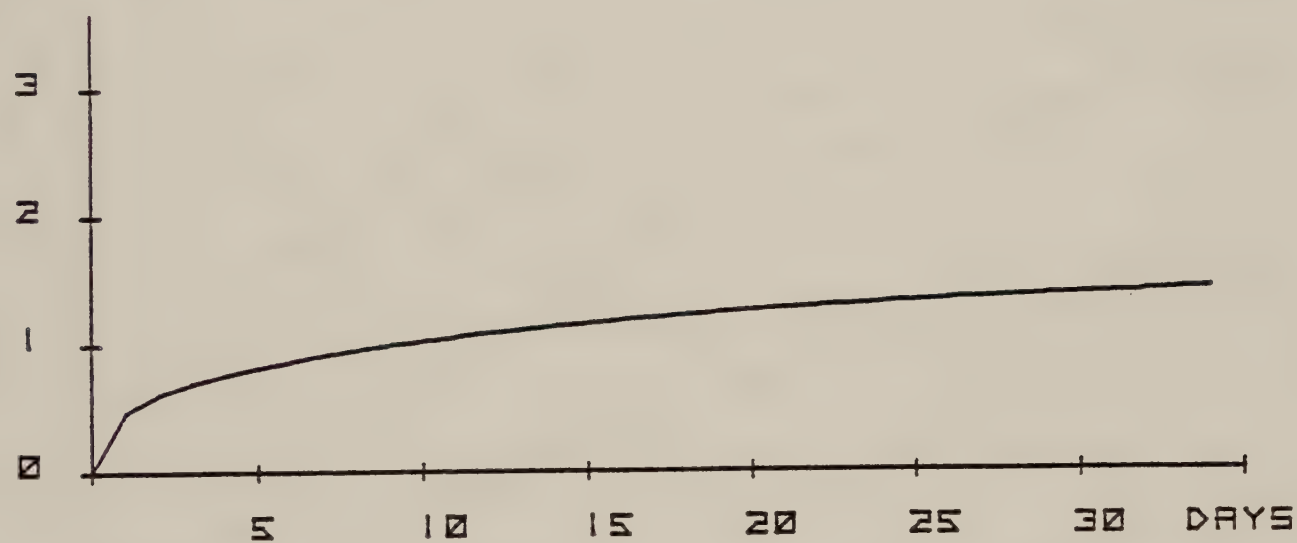
G O₂/L SEDIMENT

Fig 13) Oxygen demand (obtained with Sapromat at 20 °C) of Lake Lillesjön sediment from 4 m water depth after denitrification of added nitrate.

LAKE LILLESJÖN

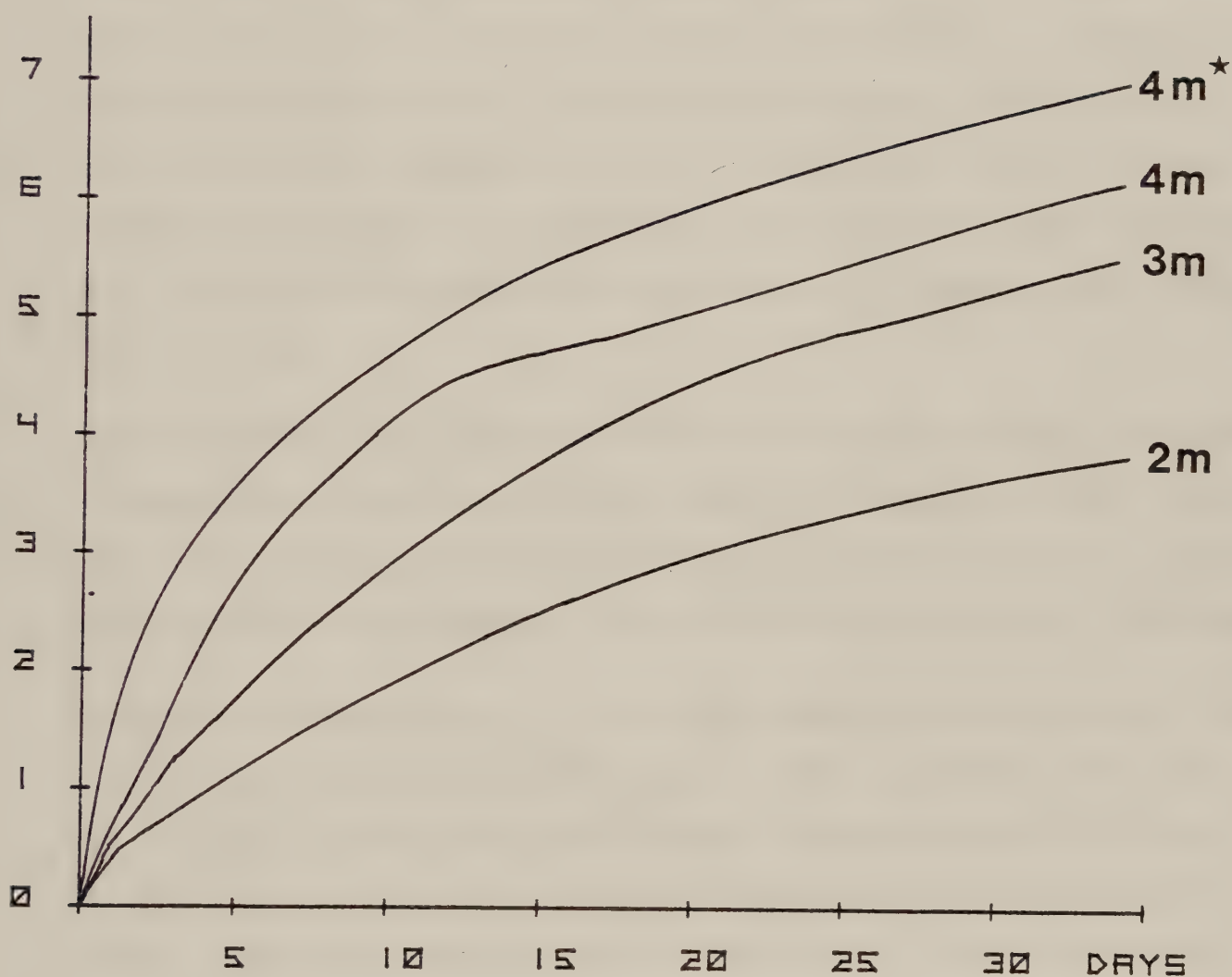
G O₂/L SEDIMENT

Fig 14) Oxygen demand (obtained with Sapromat at 20 °C) of Lake Lillesjön sediments sampled at 2 m, 3 m and 4 m water depth before restoration.

(★) sample taken 741023, all other samples were taken 740816.

The purpose of the P exchange experiments was to determine equilibrium concentrations in the water column above the sediment surface. For this reason, small water samples (10 ml) were drawn on each sampling occasion. The water removed was replaced by 10 ml bicarbonate buffer. The total water volume removed was less than 10 % of the initial water volume. P concentrations were corrected for dilution by multiplication with a factor $V/(V-10)$ where V = volume of the water initially present in ml. Results corrected in this way corresponded well with results obtained from cores analyzed only at the termination of the incubation. Sediment with nitrate added showed low phosphate concentrations in the overlying water, and no corrections were applied to the results obtained in these systems.

Concentrations of phosphate as functions of time in the experimental systems without nitrate additions were fitted to power curves using the least squares method. Power curve fitting gave a better coefficient of determination than linear or exponential functions.

Phosphate concentrations in the water phase in cores treated with nitrate stabilized at low values and showed no change with time. The outflow of phosphate from sediment cores taken at different water depths differed considerably. Two consecutive experimental series from Lake Lillesjön are illustrated in Fig 15 A and Fig 15 B. Similar experiments were also conducted with sediment cores from various lakes in Stockholm (Fig 16). In all experiments without NO_3 addition, P concentrations at the termination of the experiments were similar to the P concentrations in the interstitial water.

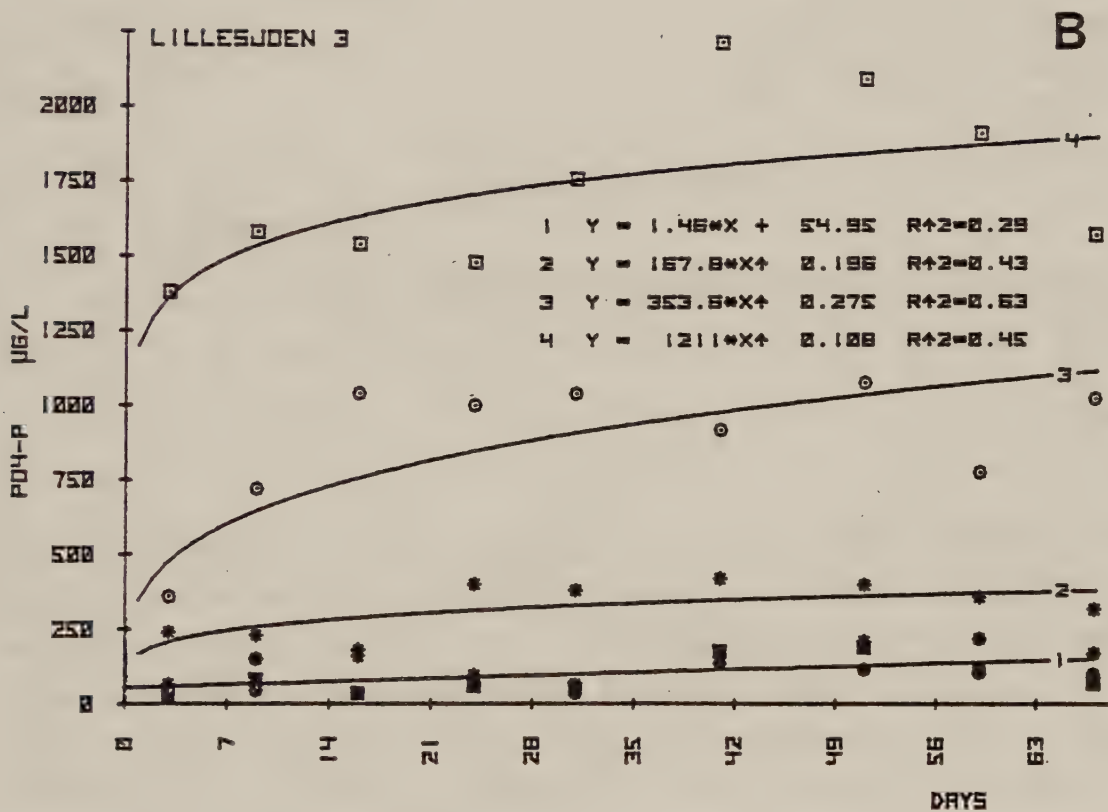
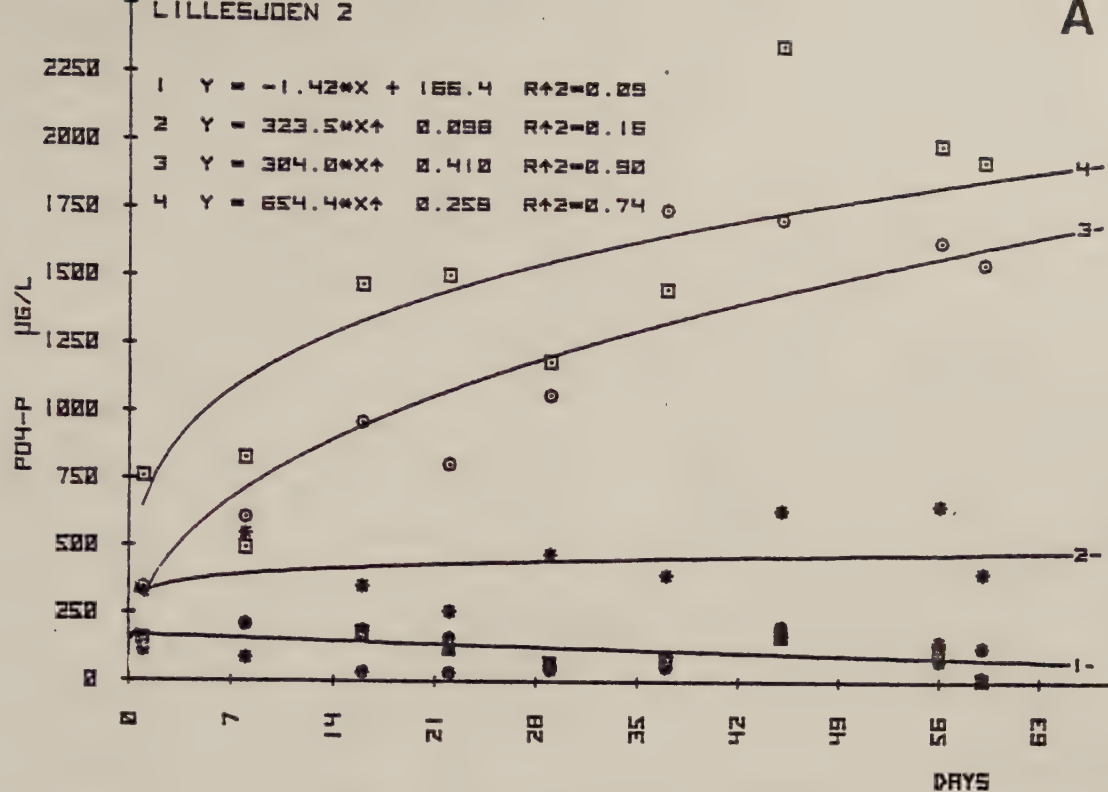


Fig 15) Phosphate concentration in water above sediment from Lake Lillesjön. Sediment cores taken at 2, 3 and 4 m water depth and incubated with (solid symbols) and without (open symbols) nitrate at 4-6 °C under anaerobic conditions. Regression line 1 represents pooled nitrate-treated samples from all depths, and regression lines 2, 3 and 4 represent sediments from 2, 3 and 4 m water depth, respectively, incubated without nitrate. A) Experimental series Lillesjön 2. B) Experimental series Lillesjön 3.

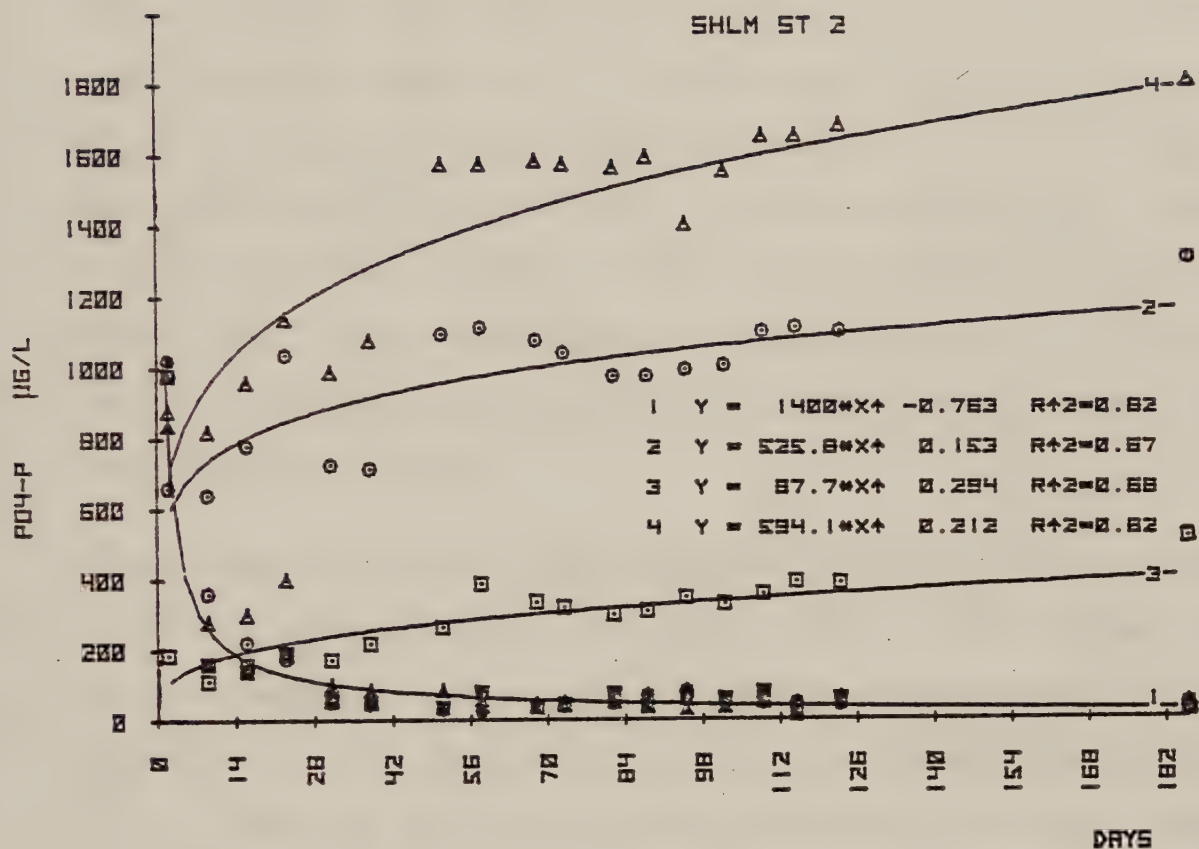


Fig 16) Phosphate concentration in water above sediment cores from Stockholm lakes incubated under anaerobic conditions at 4-6 °C. 1) regression line for pooled nitrate-treated samples from all lakes, 2) regression line for Lake Lillsjön, 3) regression line for Lake Långsjön and 4) regression line for Lake Trekanten. 2), 3) and 4) represent cores incubated without nitrate addition;

3.3.3. Denitrification studies

Favorable experimental conditions for the measurement of denitrification were achieved when the nitrate solutions were distributed evenly in the water phase and gradients were avoided by gentle stirring before sampling. A linear nitrate decrease was obtained in practically all experiments conducted in this way. Since 2-4 days were required at the start of the experiments for equilibrium to be established between nitrate concentrations in the water column and in the superficial sediment, the initial nitrate concentrations were estimated as the intersects of the linear regression lines with the y-axes.

In experiments where nitrate diffused into the sediment cores, an initial proportionality was seen between the thickness of the affected sediment layer and the nitrate concentration in the water column above. The result of one of these experiments is given in Fig 17. When the experiments were terminated, nitrate remaining in the interstitial water was still distributed over the same thickness but at lowered concentrations. The highest concentration corresponded to the concentration found in the water column above the sediment (cf. Fig 22 A).

Five series of denitrification experiments were conducted with Lake Lillesjön sediment.

1) Series 1 was conducted with sediment cores from 4 m water depth which were incubated in the dark at room temperature (23 °C). Of 6 incubated cores, 4 were discarded due to severe disturbances resulting from vigorous gas development. In the remaining two

DIFFUSION OF NITRATE INTO SEDIMENT

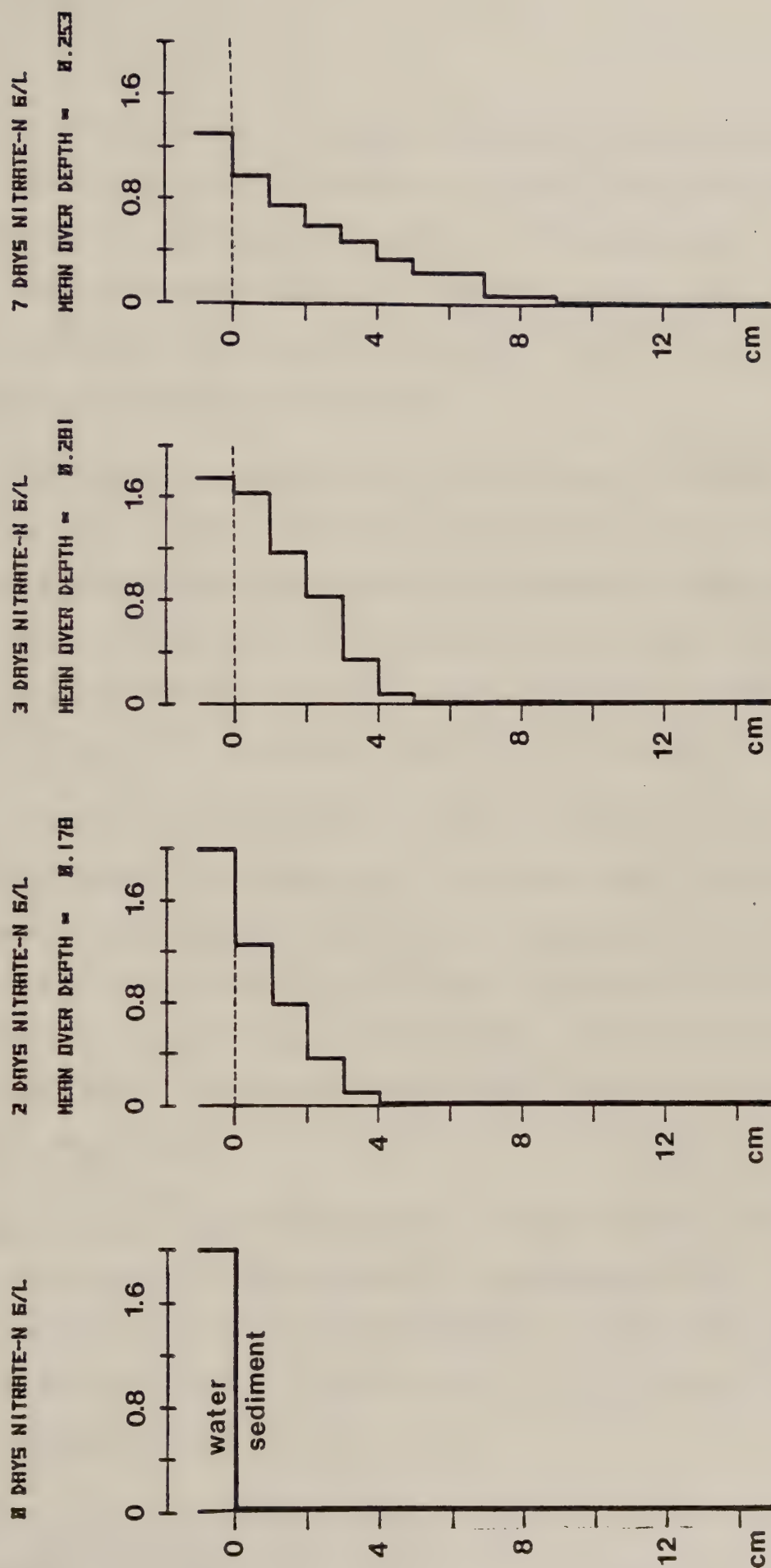


Fig 17) Diffusion of nitrate into sediment cores. Interstitial water sampled 2, 3 and 7 days after nitrate addition to the water above the sediment surface.

systems the decrease in nitrate was linear during the entire experiment (Fig 18 A). The rate of nitrate depletion was dependent on the initial nitrate concentration. The regression lines for both cores coincided when the initial concentrations were taken as 100 %. Nitrate concentrations decreased with 2.2 % of the initial concentration per day (Fig 18 B).

2-3) Experimental series 2 and 3 were almost identical in design. In these series the effects of sediment-conditioning chemicals on denitrification were determined. The sediment cores were taken at 2, 3 and 4 m depth and were incubated in the dark at 4-6 °C. 3.7 g technical Ca-nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) was added to each sediment core (140 g N/m^2) in series 2 and half this amount in series 3.

After nitrate addition a set of cores from the various water depths received further additions of 3 g CaO per core. One core taken at 4 m water depth was incubated with nitrate, CaO (3 g) and 0.9 g Fe as FeCl_3 . Expressed on a m^2 basis, the additions in series 2 amounted to 1 kg Ca-nitrate (technical), 0.8 kg CaO and 1.3 kg technical FeCl_3 (15 % Fe w.w.) solution. In series 3 half these amounts were added.

Sediment cores from different water depths showed similar denitrification rates when calculated on a percentage basis. The mean rates obtained for the two experimental series were 0.81 %/d and 0.74 %/d, respectively, with a mean of 0.77 %/d or 35 % of the rates obtained at 22-24 °C.

Addition of CaO increased denitrification rates with 10-15 %, and additions of CaO and FeCl_3 gave a c. 20 % increase (Fig 19 A-C, Fig 20 A-C).

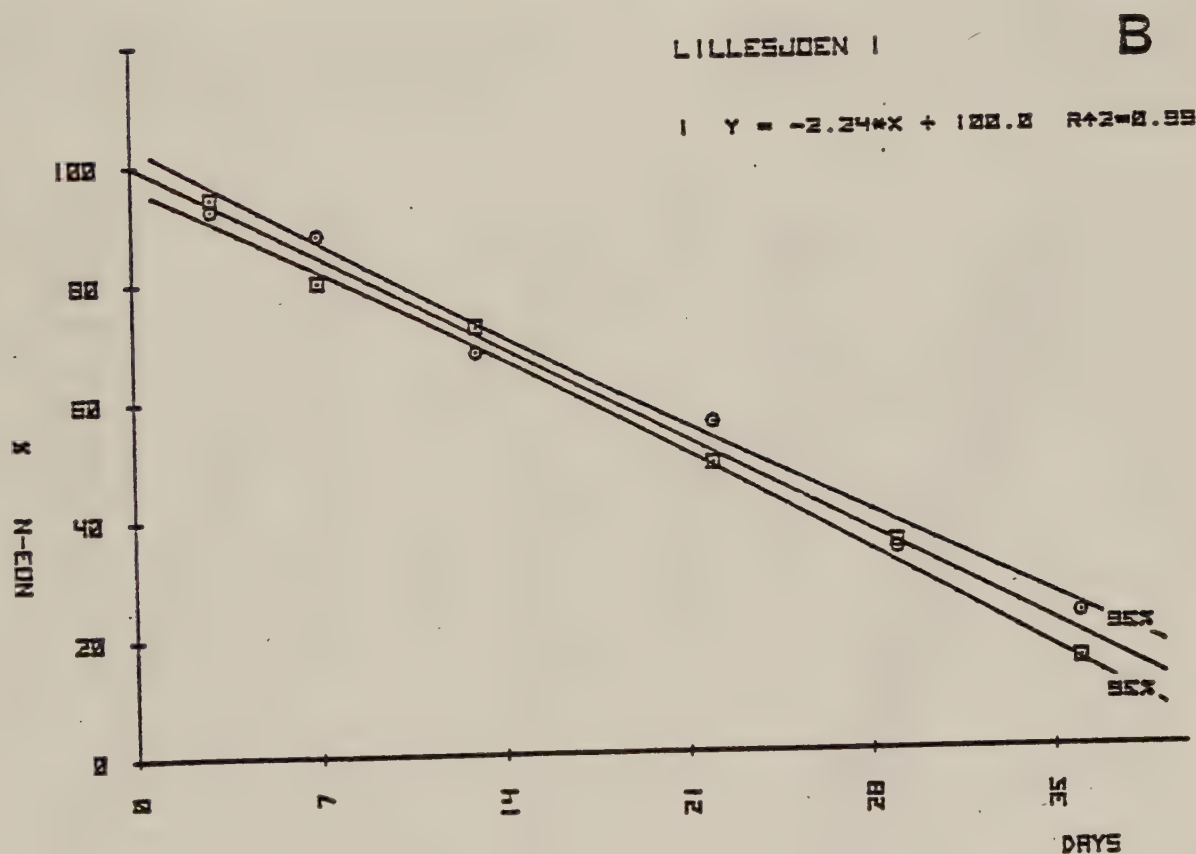
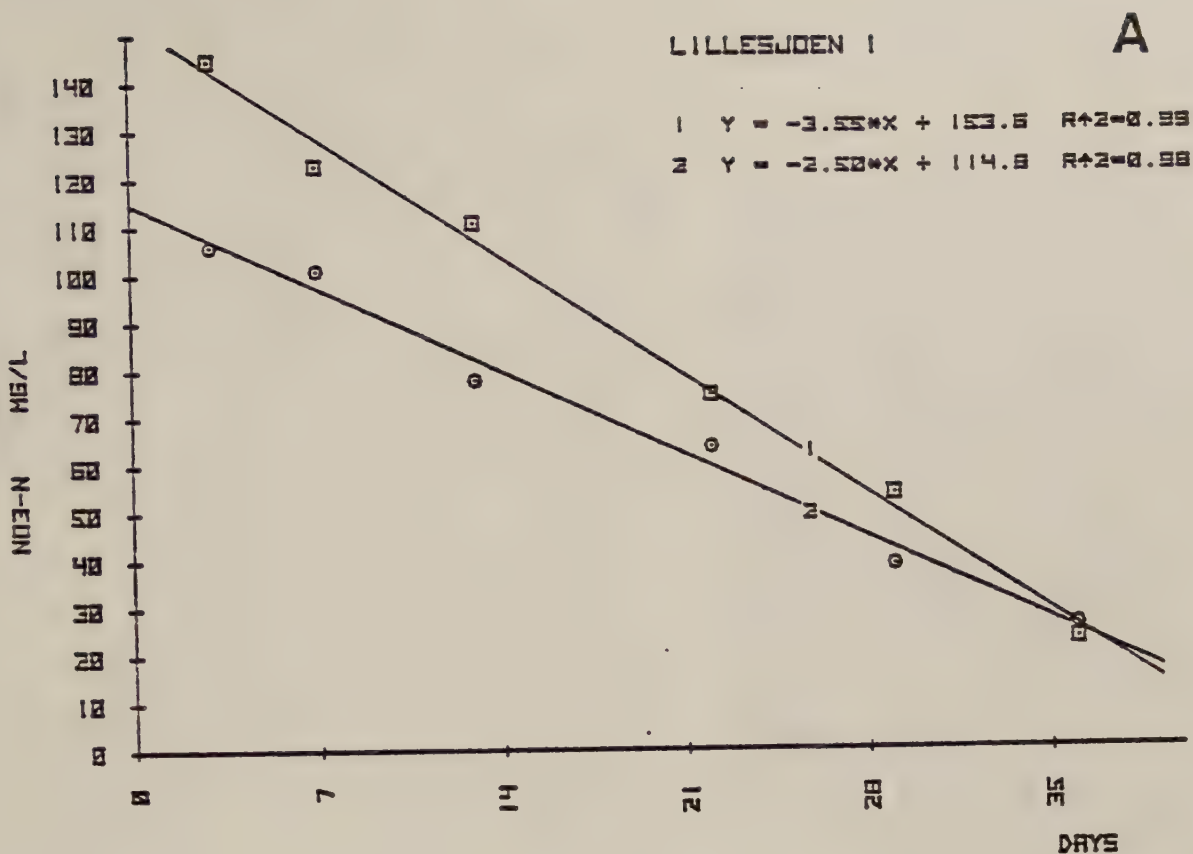


Fig 18) Experimental series Lillesjön 1. A) Nitrate concentration in water above sediment. Two sediment cores from 4 m water depth were incubated anaerobically at 22-24 °C. In core 1 (□) the initial nitrate concentration was 154 mg N/l, in core 2 (o) 115 mg N/l. B) Results expressed as % of initial concentrations.

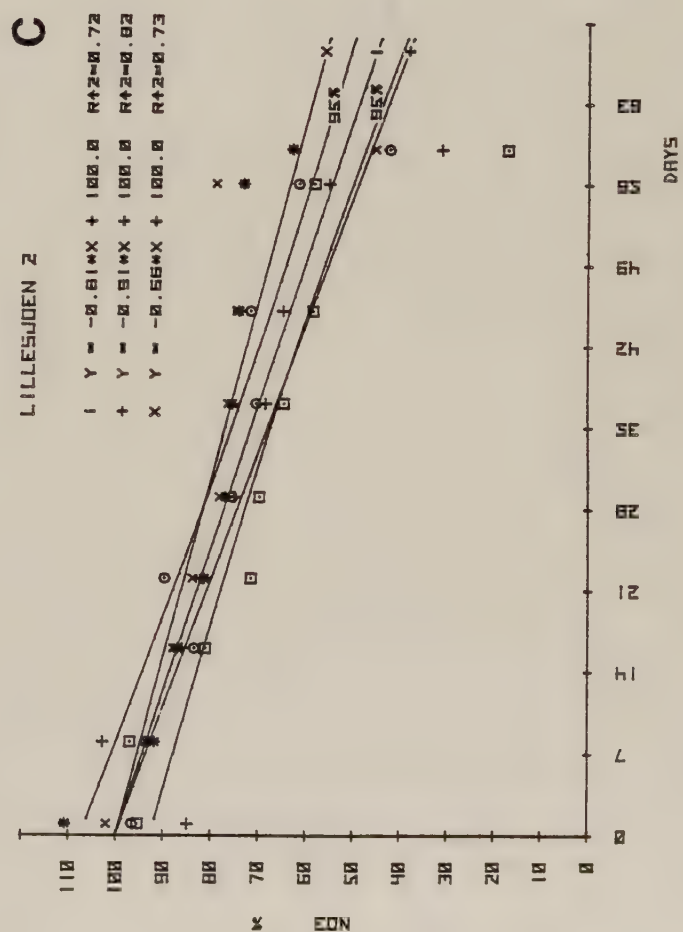
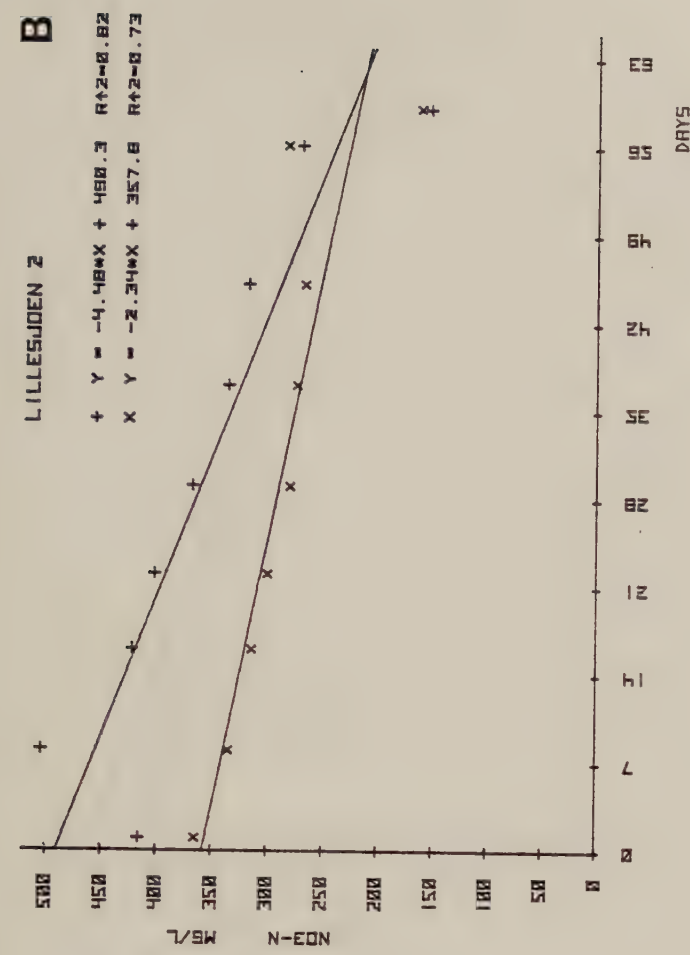
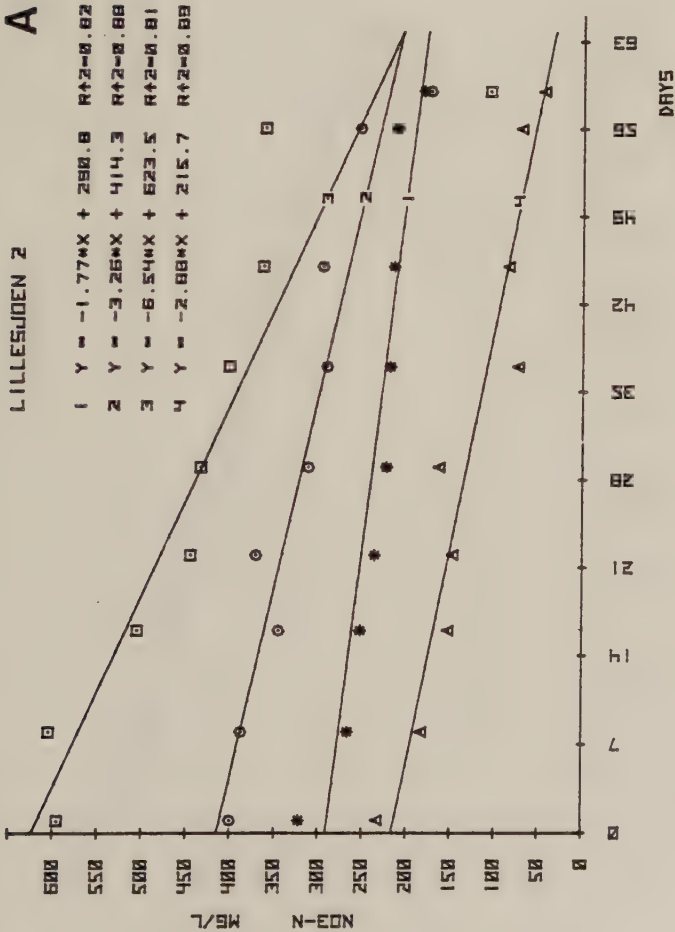


Fig 19) Experimental series Lillesjön 2. Nitrate concentration in water above sediment cores incubated anaerobically at 4-6 °C. Symbols and regression lines: A) Sediment from 2 m water depth (★,1), 3 m (○,2) and 4 m (□,3). Sediment from 4 m with iron and lime addition (△,4). B) Sediment from 4 m with (+) and without (x) lime addition. C) Results expressed as % of initial nitrate concentrations. Data from sediment taken at 2, 3 and 4 m water depth (symbols as in A) are pooled for calculation of regression line (1) with 95 % confidence interval. Data and regression lines ("+" and "x") from B) are also included.

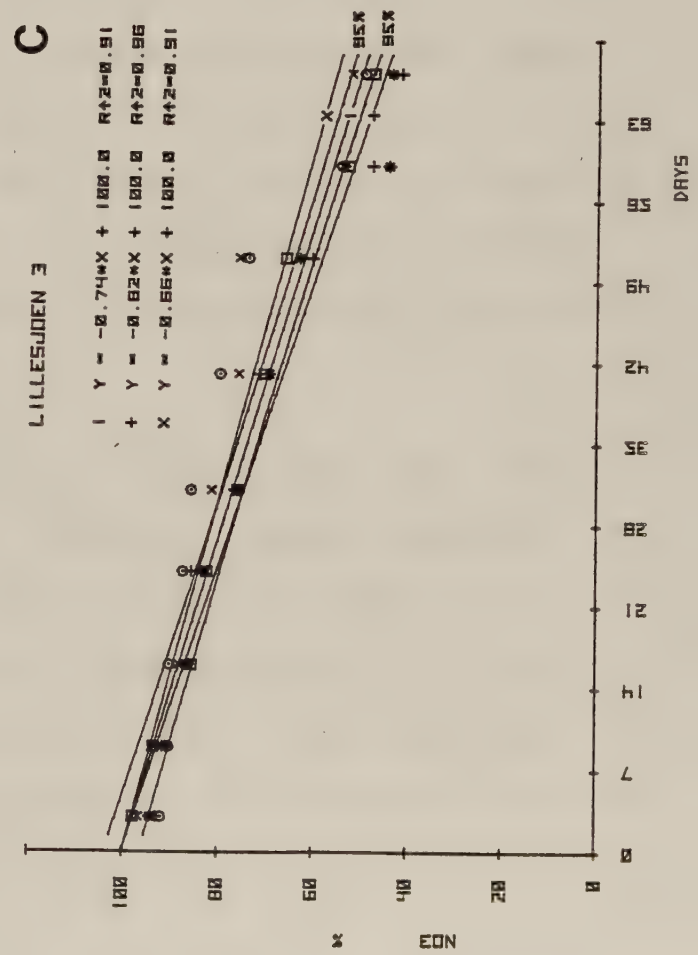
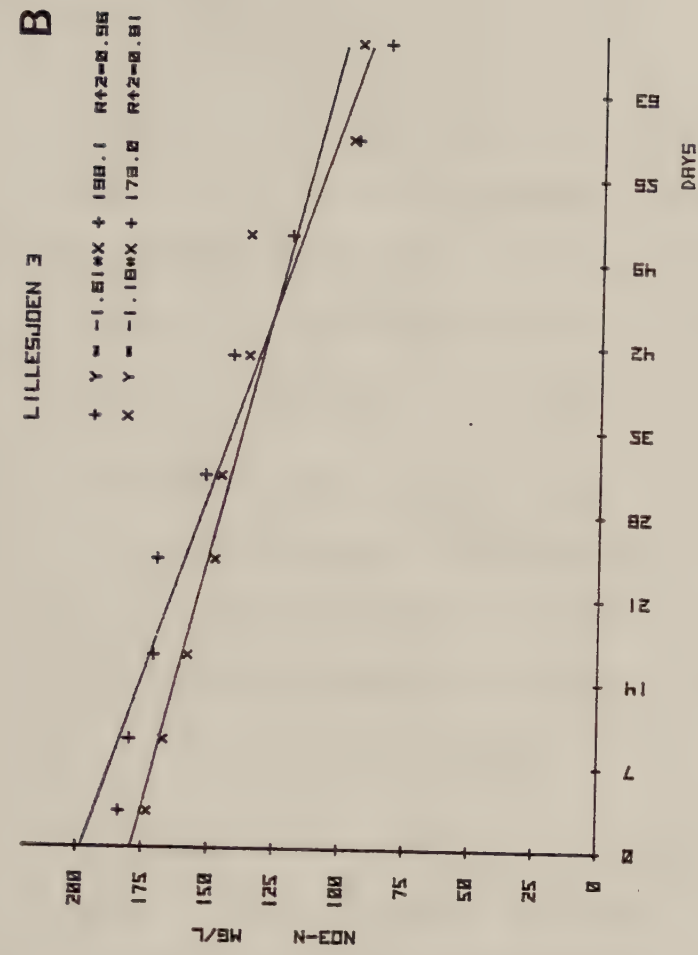
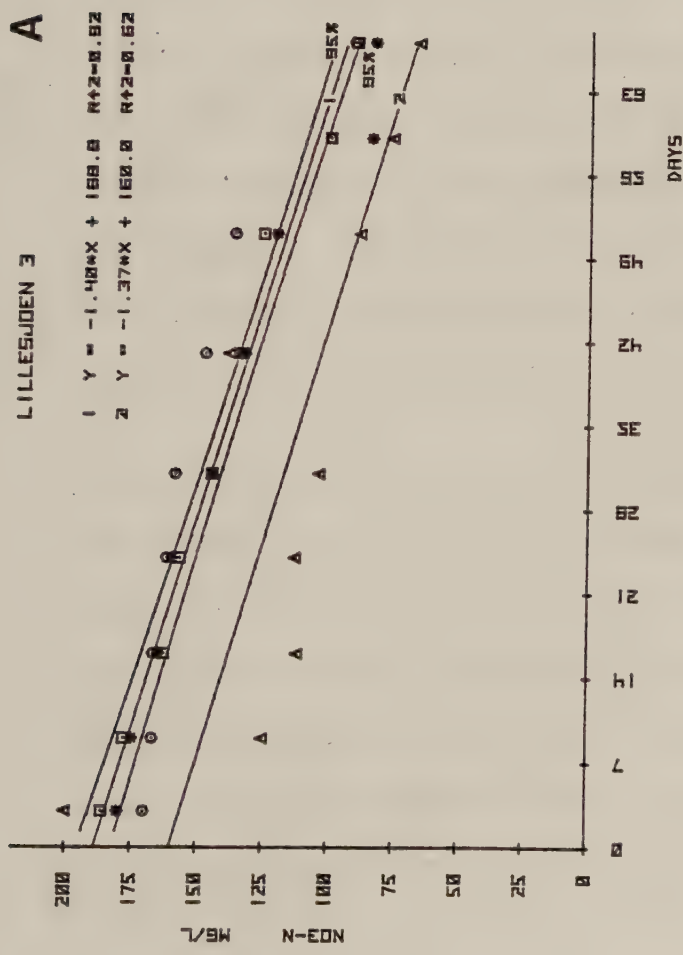


Fig 20) Experimental series Lillesjön 3. Nitrate concentration in water above sediment cores incubated anaerobically at 4-6 °C. Symbols and regression lines: A) Sediment from 2 (★), 3 (○) and 4 (□) m water depth. Regression line 1 with 95 % confidence interval computed from all depths pooled. (Δ) and regression line 2 represent nitrate concentrations in a core taken at 4 m water depth and treated with iron and lime. B) Sediment from 4 m water depth with (+) and without (x) lime addition. C) Results expressed as % of initial nitrate concentrations. Data from sediment taken at 2, 3 and 4 m water depth (symbols as in A) are pooled for calculation of regression line (1) with 95 % confidence interval. Data and regression lines ("+" and "x") from B) are also included.

Chemical analyses after termination of experiments with 2 sediment cores (4 m water depth) without additions and with CaO and NO_3 added are given in Fig 21 A and B). Analyses of interstitial water in 2 experimental cores (4 m water depth), one with nitrate addition and one with no additions, are given in Fig 22 A and B.

4) Experimental series 4 was conducted to

- a) investigate differences in denitrification patterns of stratified and completely stirred systems, and
- b) measure denitrification rates in systems open to air and partially aerated.

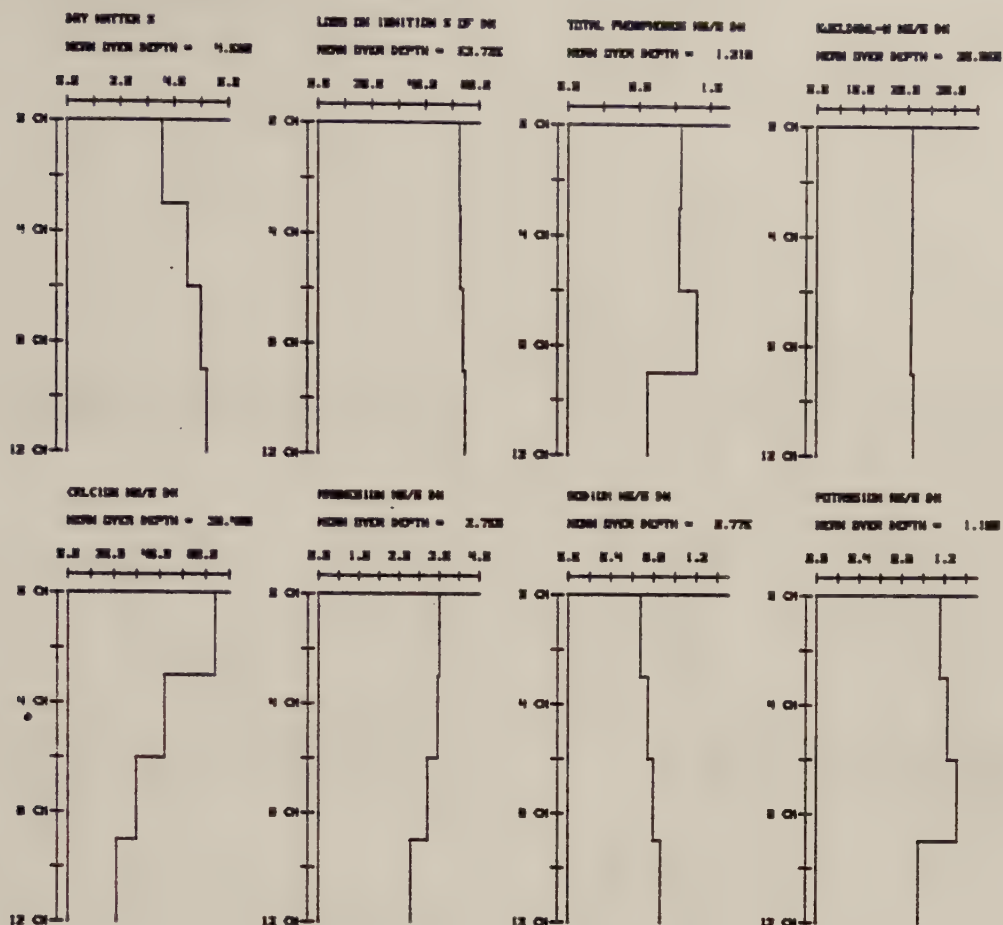
In experimental series 4 a, four 2.5 liter bottles were filled with 1 liter sediment each and 1.5 liters lake water. 11.2 g Ca-nitrate was added (535 mg N/l). The bottles were thoroughly shaken twice a day and the sum nitrite + nitrate was determined twice a week. The results showed some scatter due to disturbances in the nitrate analysis (some samples were coloured or turbid in spite of filtration). The results from all experimental systems combined gave similar denitrification rates to those obtained in the core experiments (1.07 %/d) (Fig 23).

Experimental series 4 b was conducted with sediment cores from 4 m water depth, open to the air. The water was additionally aerated 5 minutes every day by bubbling with air immediately above the sediment surface. Initial additions were 11.2 g Ca-nitrate to three cores and 3.7 g Ca-nitrate to the remaining three. Denitrification rates were 0.42 %/d for the cores with the higher additions and 0.32 %/d for the lower (Fig 24).

TERMINATION OF L1 EXP #2 SEDIMENT

CORE WITH NITR AND CHD ADDED

A



TERMINATION OF L1 EXP #2 SEDIMENT

REFERENCE CORE

B

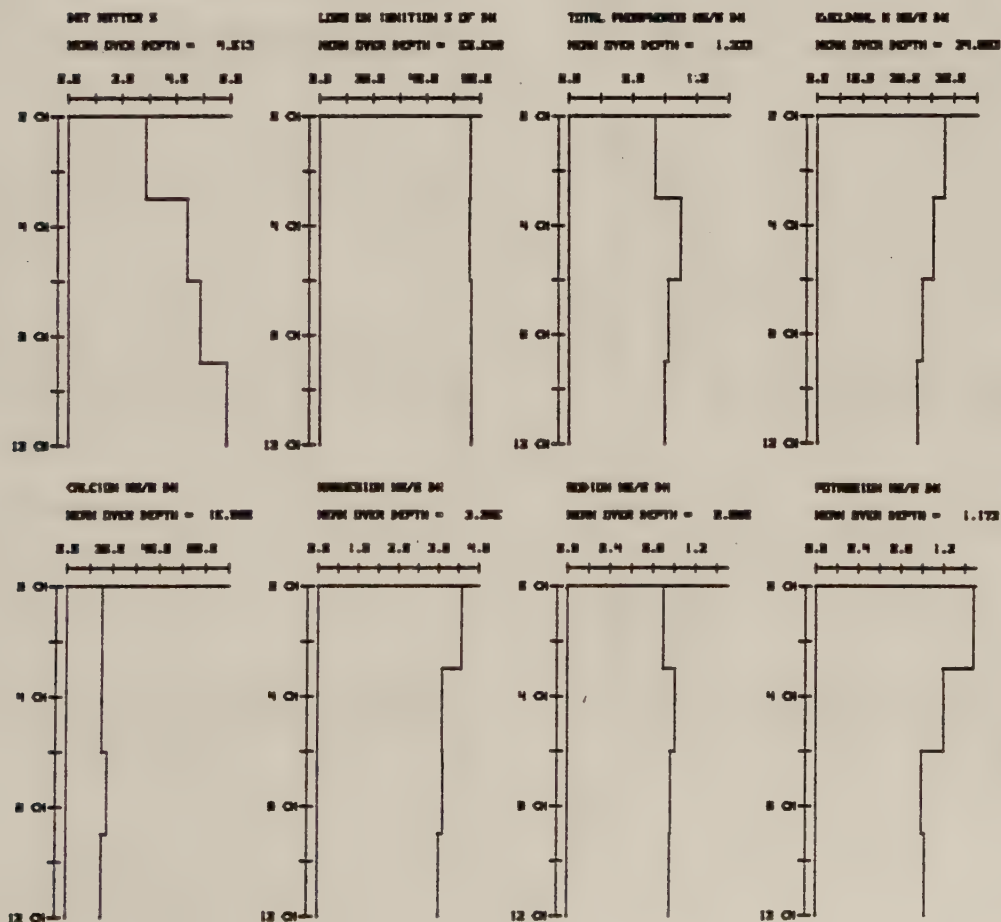
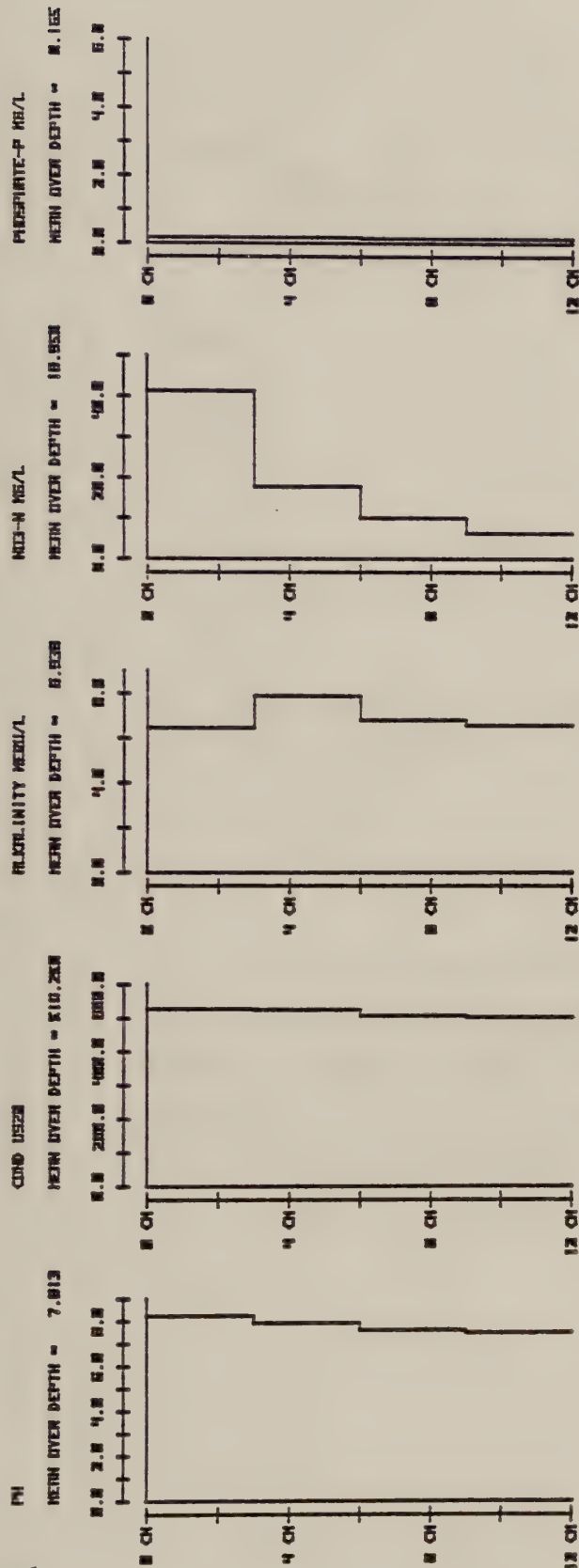


Fig 21) Vertical distribution of various parameters in Lake Lillesjön sediment at termination of experimental series 2. Sediment cores from 4 m water depth incubated anaerobically. A) Nitrate added, B) Reference core without nitrate addition.

A



B

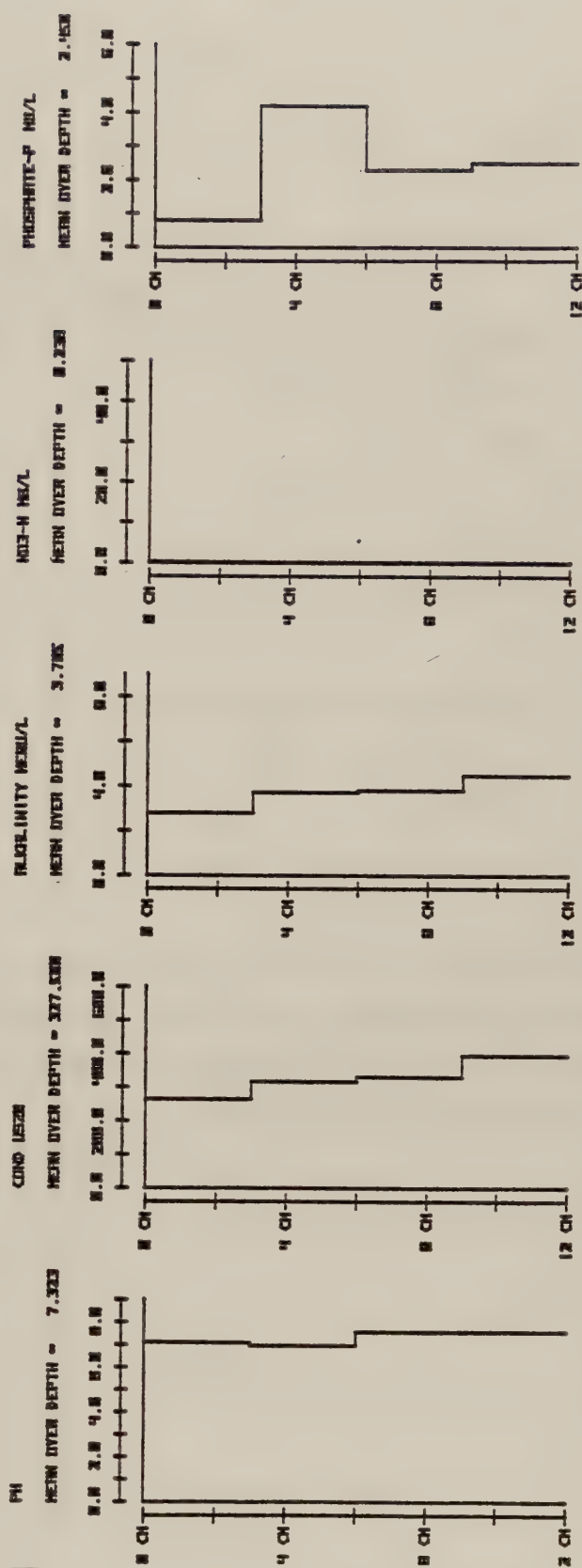


Fig 22) Vertical distribution of various parameters in Lake Lillesjön sediment interstitial water from 4 m water depth at termination of experimental series 2. Cores incubated anaerobically. A) Nitrate added. B) Reference core without nitrate addition.

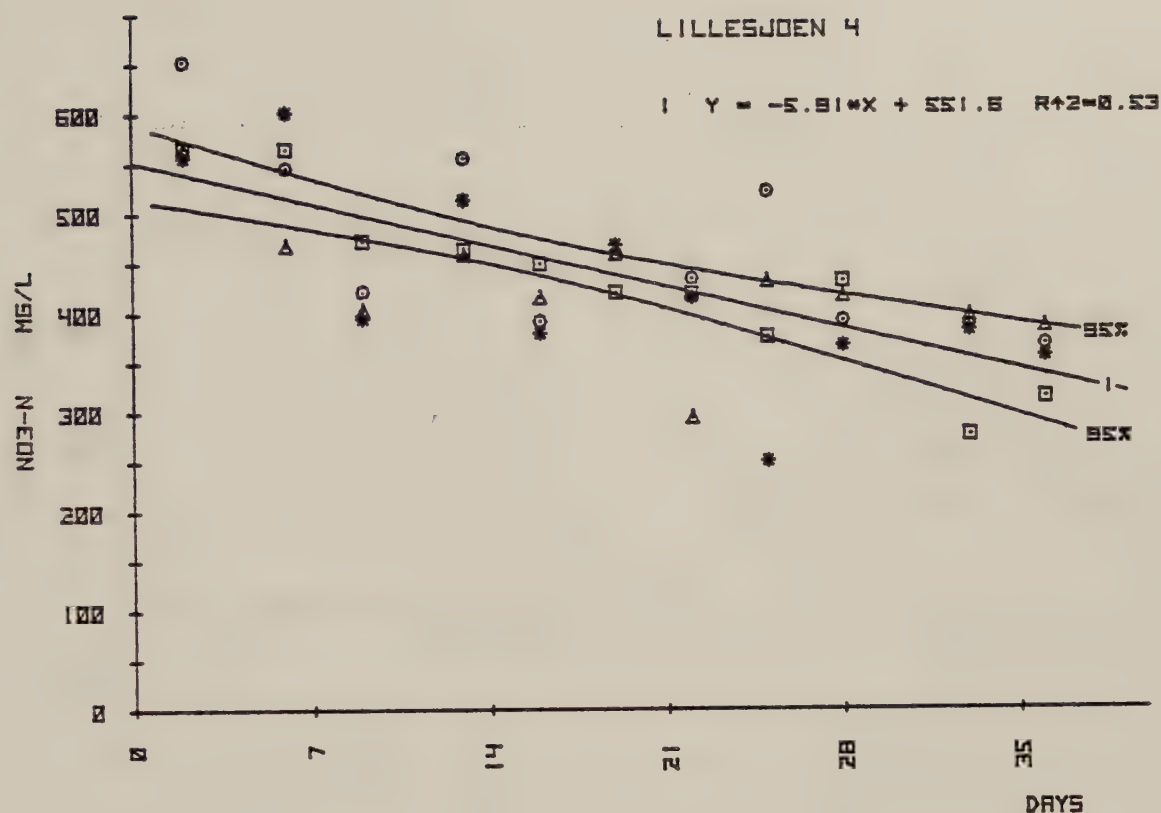


Fig 23) Experimental series Lillesjön 4a. Nitrate concentrations in 4 identical experimental systems containing sediment and water from 4 m water depth. Bottles shaken daily and incubated anaerobically at 4-6 °C. All data were pooled when the regression line and 95 % confidence interval were computed.

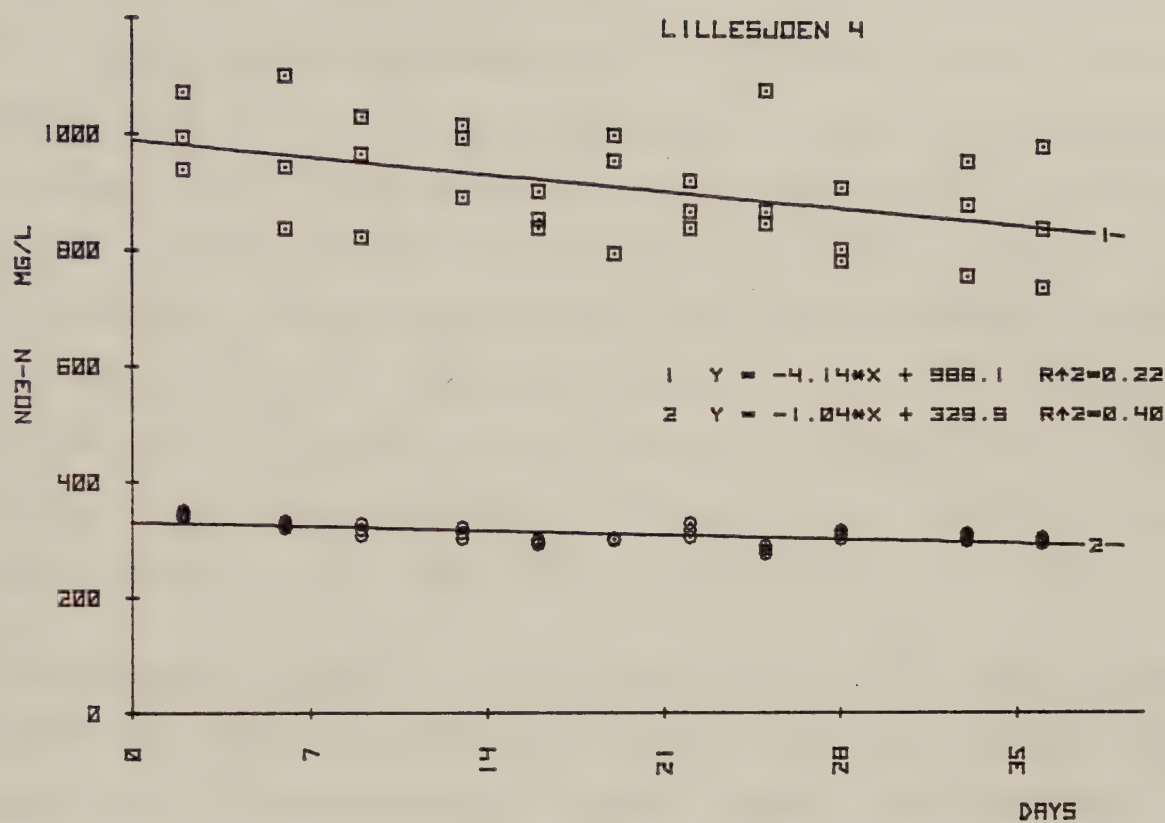


Fig 24) Experimental series Lillesjön 4b. Nitrate concentrations in aerated water above sediment cores incubated at 4-6 °C. ($\square$,1) Data and regression line from 3 sediment cores from 4 m water depth with initial nitrate concentrations of 1000 mg N/l; ($\circ$,2) Data and regression line from 3 sediment cores from 4 m with initial nitrate concentrations of 330 mg N/l.

5) Experimental series 5 was carried out on sediment taken in Lake Lillesjön 3 weeks after nitrate had been added to the sediment in the full-scale experiment. The sediment cores (4 m water depth) were incubated at room temperature and at 5 °C in the dark. Nitrate concentrations in the cores incubated at room temperature (23 °C) decreased linearly at first to a nitrate-N concentration of 10 mg N/l, while an exponential model gave a better fit to the data below 10 mg N/l. The linear rate of nitrate depletion was 2.3 %/d at 23 °C, which is in accordance with the results from series 1. The rate obtained at 5 °C (0.71 %/d) agrees with experimental series 2 and 3 (Fig 25 A).

In experimental series 5 the gas evolved from the cores was collected, measured and analyzed. The gas consisted of between 93 and 96 % N₂, trace amounts of oxygen + argon (not separated in the chromatogram, and 4-7 % CO₂ + CH₄. The N₂ evolved corresponded to the nitrate consumed (Fig 25 B and C). Phosphate concentrations were monitored in the experimental cores (Fig 25 D).

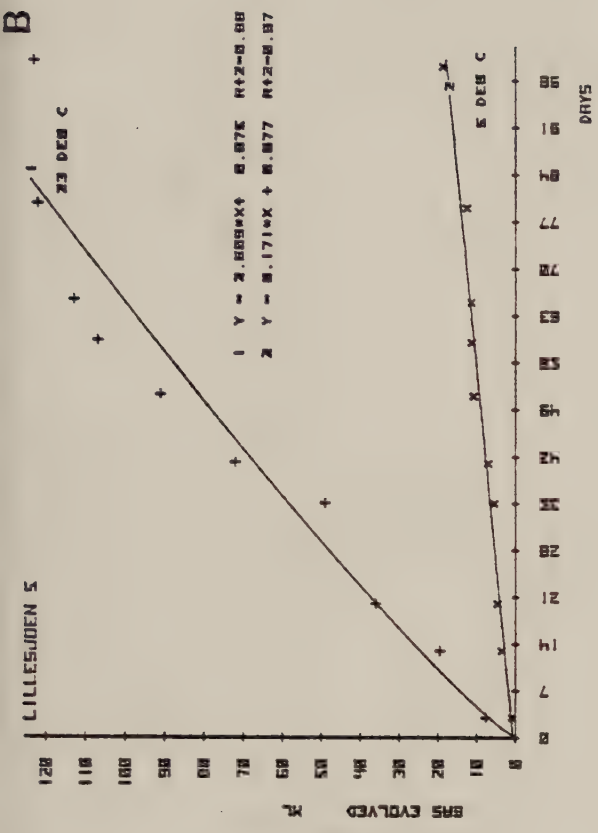
Denitrification rates in sediments from other former sewage recipients were determined in the same way as in the sediments from Lake Lillesjön. Characteristics of the sediments treated are given in Table 2.

Sediment cores from 4 lakes in Stockholm (Laduviken, Lillsjön, Långsjön and Trekanten) were incubated with Ca-nitrate in 2 consecutive series (Fig 26 and 27 A and B). The denitrification rates obtained were somewhat lower and more scattered than the rates obtained for Lake Lillesjön sediment.

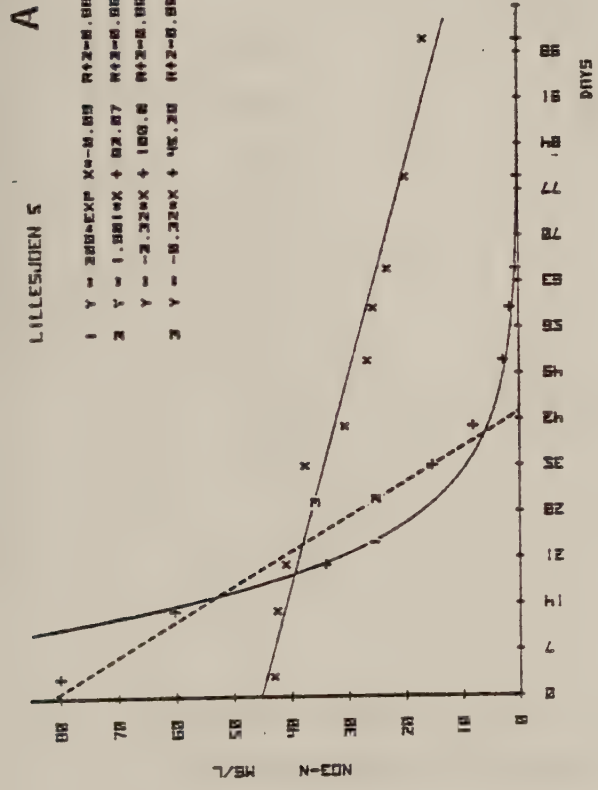
Table 2) Characteristics of lake sediments in the Stockholm region.

	LADUVIKEN	LILLSJÖN	LÅNGSJÖN	TREKANTEN	FLATEN
SEDIMENT					
Dry matter %	4.3	10.1	7.3	8.3	4.5
Loss on ignition %	40.8	25.3	34.5	30.8	40.0
Acid insoluble %	35.9	53.9	44.0	36.4	49.3
Tot P mg/g d.m.	1.42	0.50	1.23	1.35	0.73
Tot N mg/g d.m.	23.4	14.3	18.8	16.1	19.3
Ca mg/g d.m.	39.1	11.1	11.1	75.3	9.8
Mg mg/g d.m.	7.1	10.6	9.5	2.5	7.4
Na mg/g d.m.	5.4	1.6	1.0	6.1	0.8
K mg/g d.m.	6.9	11.2	9.6	5.4	7.6
Fe mg/g d.m.	19.5	24.9	28.7	30.4	30.6
Mn mg/g d.m.	0.47	0.63	0.61	0.70	0.55
INTERSTITIAL WATER					
PO ₄ -P mg/l	1.22	3.23	0.57	3.70	1.43
NH ₄ -N mg/l	40.0	36.1	30.2	46.9	14.4

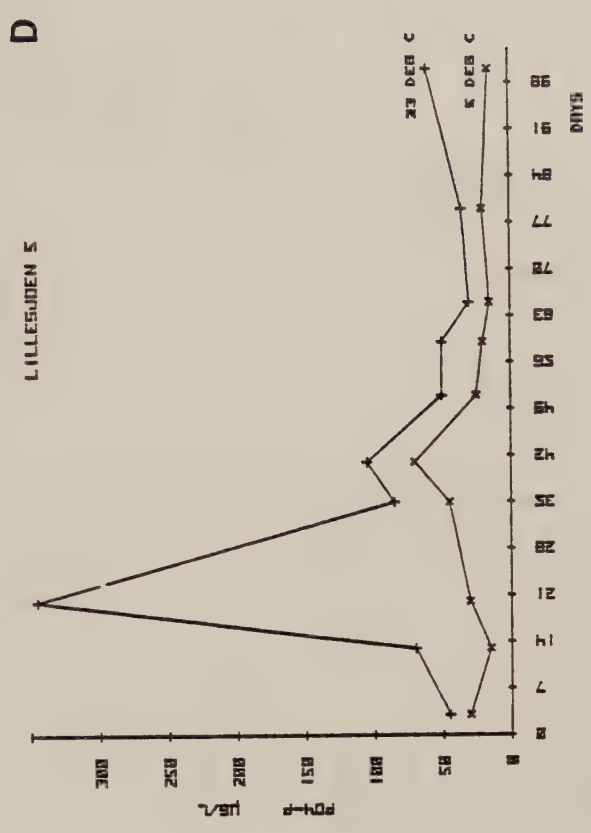
B



A



D



C

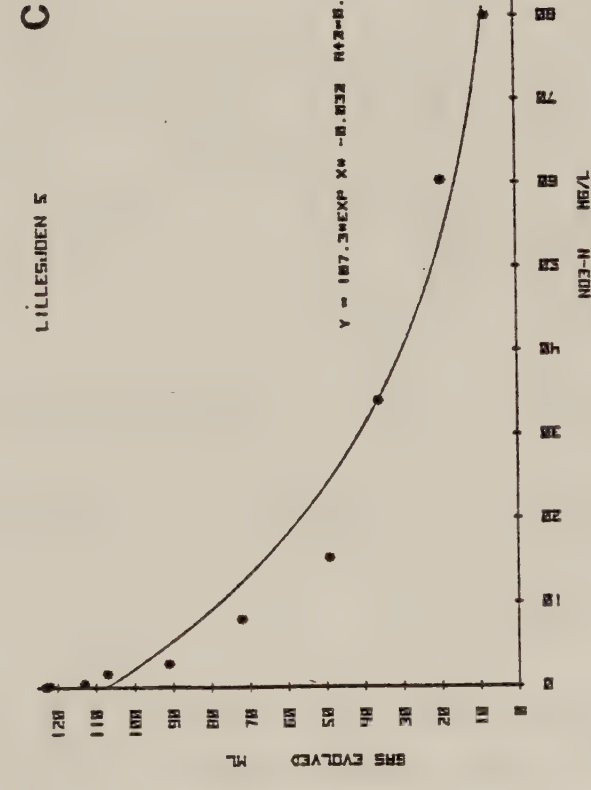


Fig 25) Experimental series Lillesjön 5. A) Nitrate concentration in water above sediment cores from 4 m water depth after nitrate application to the sediment. Anaerobic incubation. Temperatures 23 °C (+) and 5 °C (x). Regression lines for 23 °C calculated (1) for the whole period with an exponential model and (2) for the first 42 days of incubation with a linear model. Regression line for 5 °C (3) with a linear model for the entire period. B) Gas release in ml from cores incubated at 23 °C (+) and 5 °C (x). C) Relation between nitrate concentrations above the sediment core (23 °C) and gas evolved in ml. D) Phosphate concentrations in water above the sediment cores during incubation.

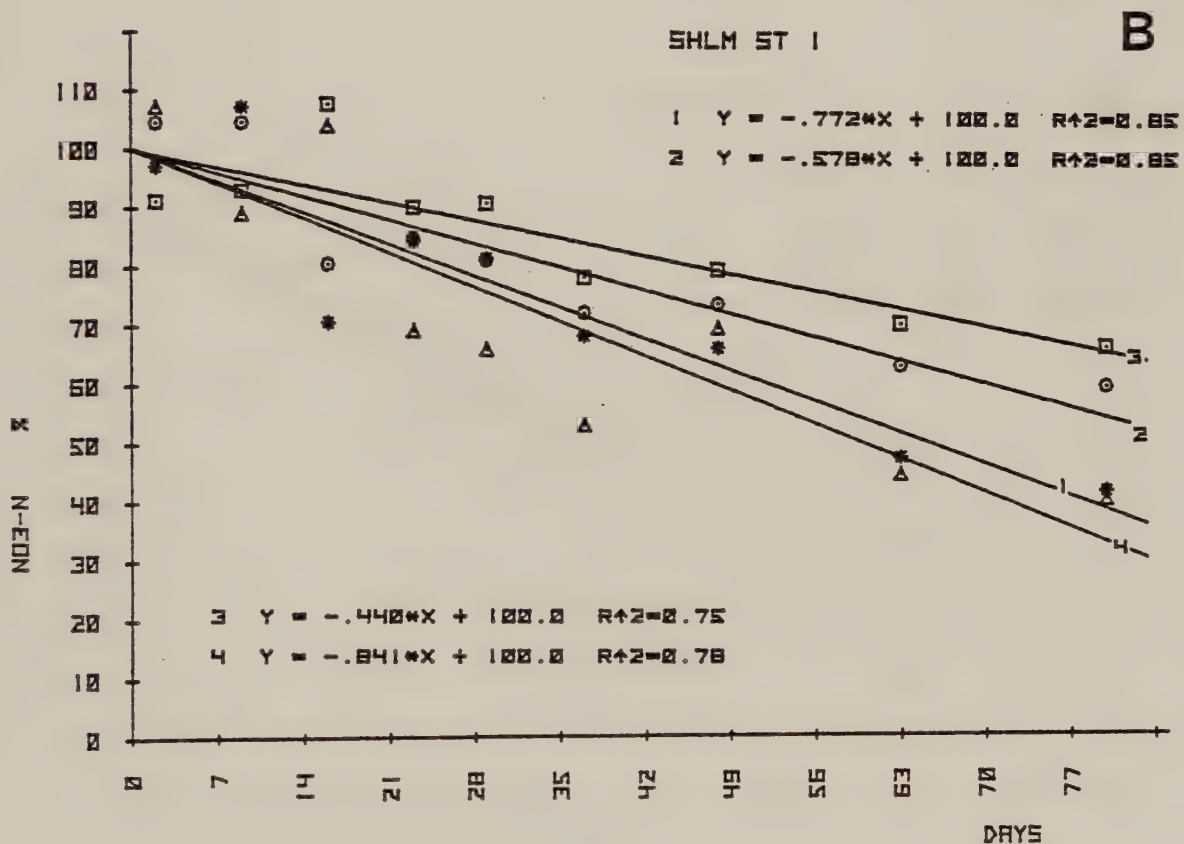
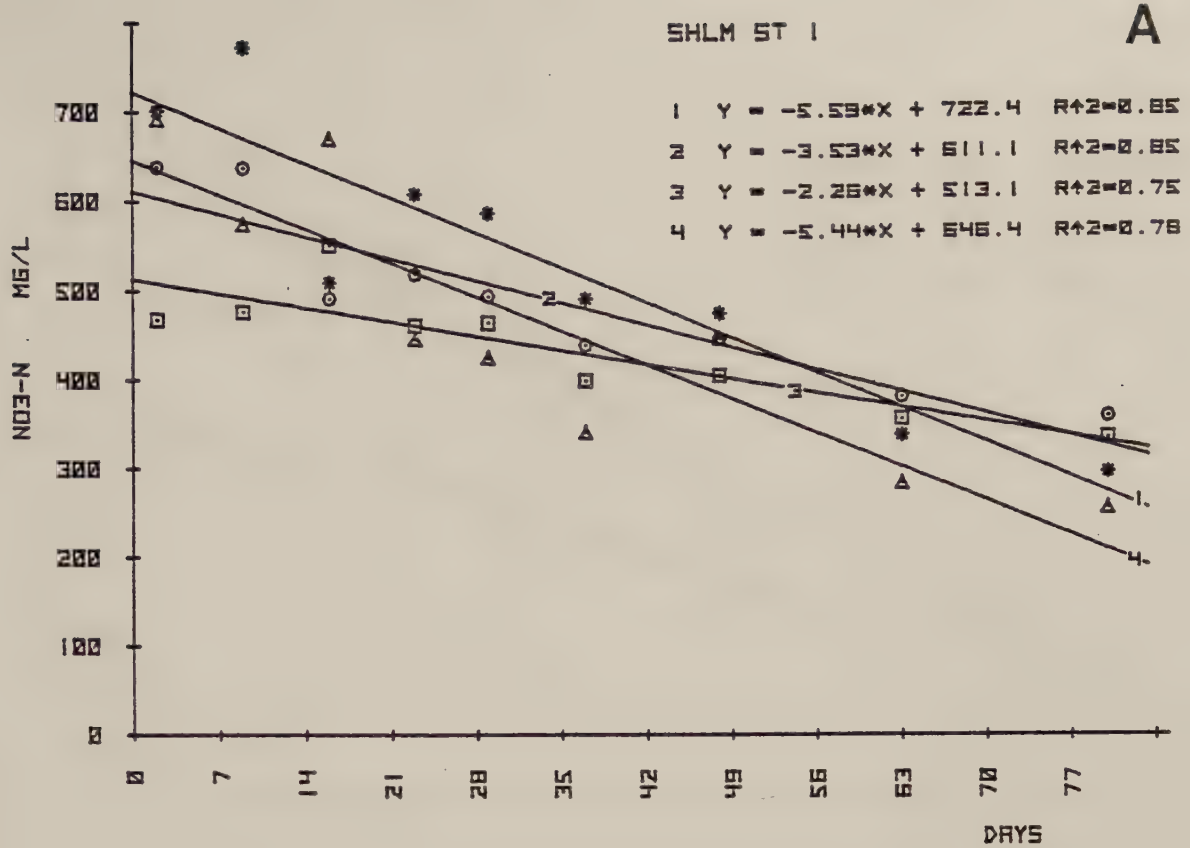


Fig 26) Experimental series Stockholm 1. A) Nitrate concentrations in water above sediment cores incubated anaerobically at 4-6 °C. Symbols and regression lines: Lake Laduviken (★,1), Lake Lillsjön (○,2), Lake Långsjön (□,3) and Lake Trekanten (△,4). B) Results expressed in % of initial nitrate concentrations.

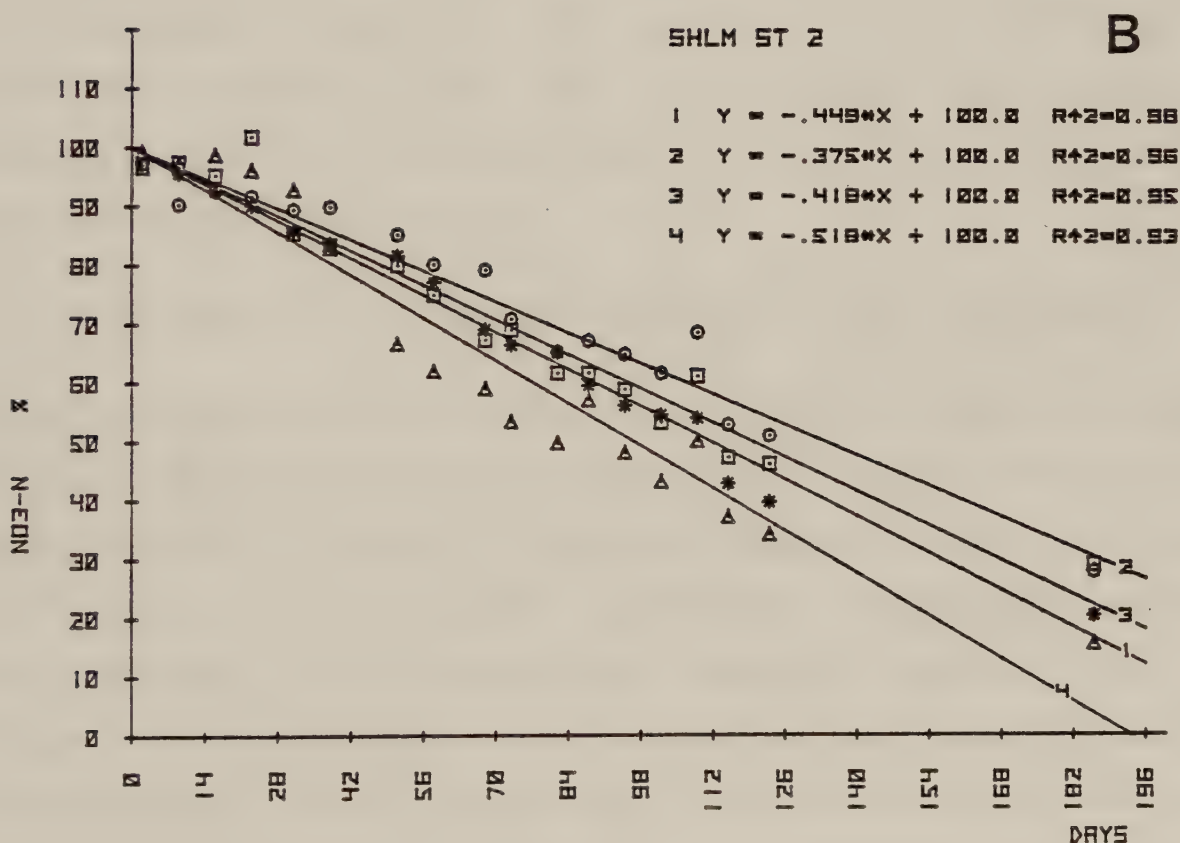
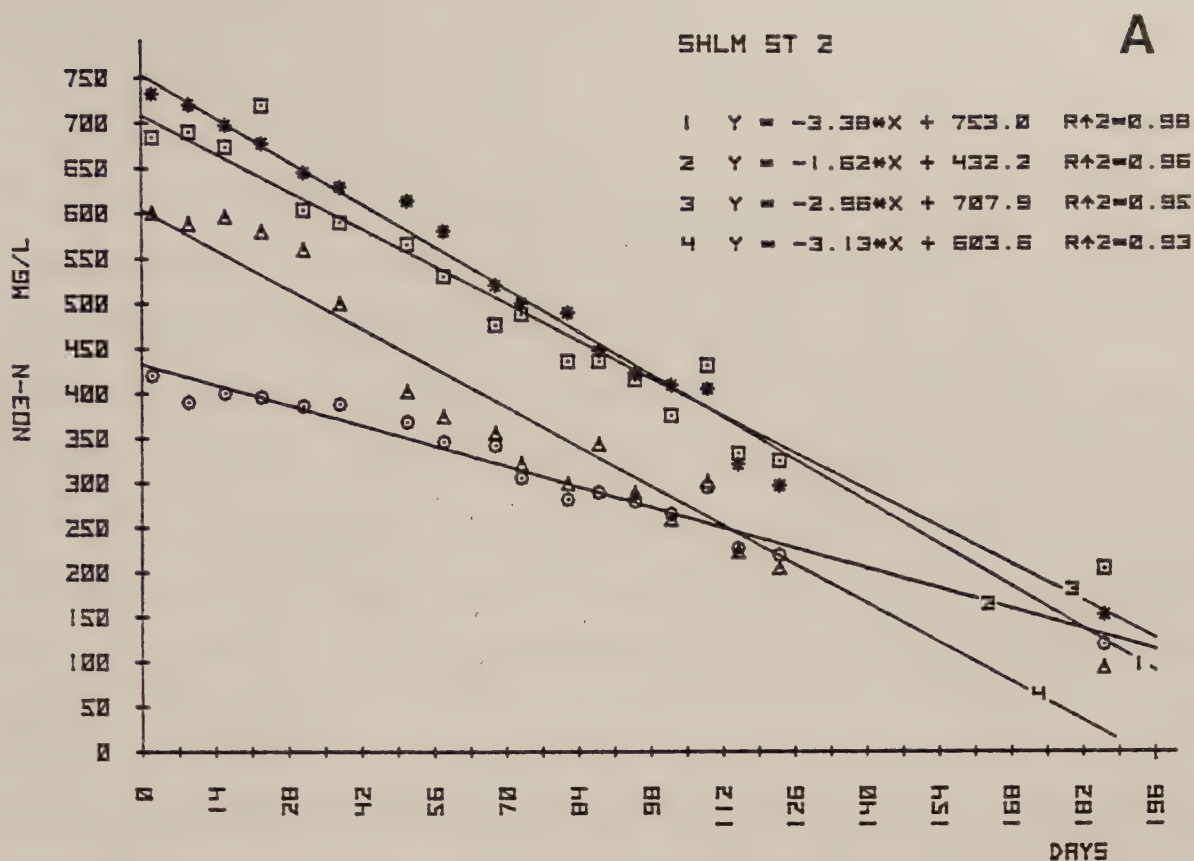


Fig 27) Experimental series Stockholm 2. A) Nitrate concentrations in water above sediment cores incubated anaerobically at 4-6 °C. Symbols and regression lines: Lake Laduviken (★,1), Lake Lillsjön (○,2), Lake Långsjön (□,3) and Lake Trekanten (△,4). B) Results expressed in % of initial nitrate concentrations.

The effects of different nitrate additions to sediment cores were investigated in sediment taken from Lake Flaten (cf. Table 2). A high degree of linearity in nitrate decrease was observed for the different initial nitrate concentrations. In these experiments nitrite was also monitored. Nitrite concentrations were related to nitrate concentrations. The maximum concentrations of nitrite were obtained between the 10th and the 40th day of incubation and did not exceed 3 % of the nitrate concentrations simultaneously present (Fig 28 A).

Although different amounts of nitrate were added to the sediment cores from Lake Flaten, similar denitrification rates were obtained on a percentage basis (0.71 %/d) at 4-6 °C. Nitrate additions on a m^2 basis were 46 g, 92 g, 137 g and 184 g N/m^2 , and rates of denitrification on a m^2 basis were 320 mg, 650 mg, 970 mg and 1310 mg $N/m^2 \cdot d$ (Fig 29 A and B).

3.3.4. Effects of the chemicals added on benthic organisms

Sediment cores from various lakes containing chironomids, tubificids and Chaoborus spp were treated with 10 g Ca-nitrate and incubated at 23 °C and 4-6 °C. At both temperatures the chironomids died within one week. However, tubificids and Chaoborus survived the treatment. Both tubificids and Chaoborus larvae burrowed deeper into the sediment, thereby avoiding high chemical concentrations close to the surface. When iron and slaked lime were added to the experimental systems with tubificids and Chaoborus larvae, only Chaoborus survived. In some experimental cores (Lake Lillesjön 2 and 3) a few specimens of tubificids survived the

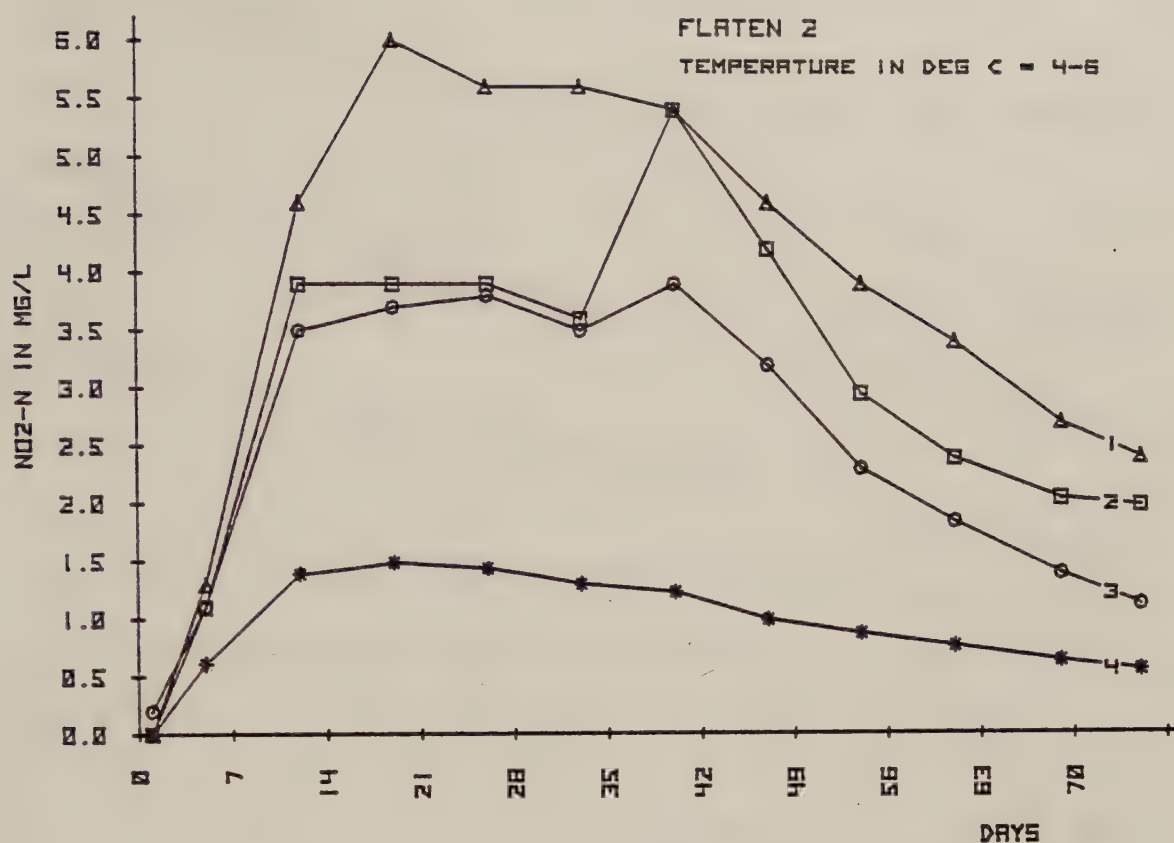


Fig 28) Experimental series Flaten 2. Nitrite concentrations in water above sediment cores incubated anaerobically at 4-6 °C with different initial nitrate concentrations: (1) 390 mg NO₃-N/l, (2) 265 mg NO₃-N/l, (3) 160 mg NO₃-N/l and (4) 55 mg NO₃-N/l.

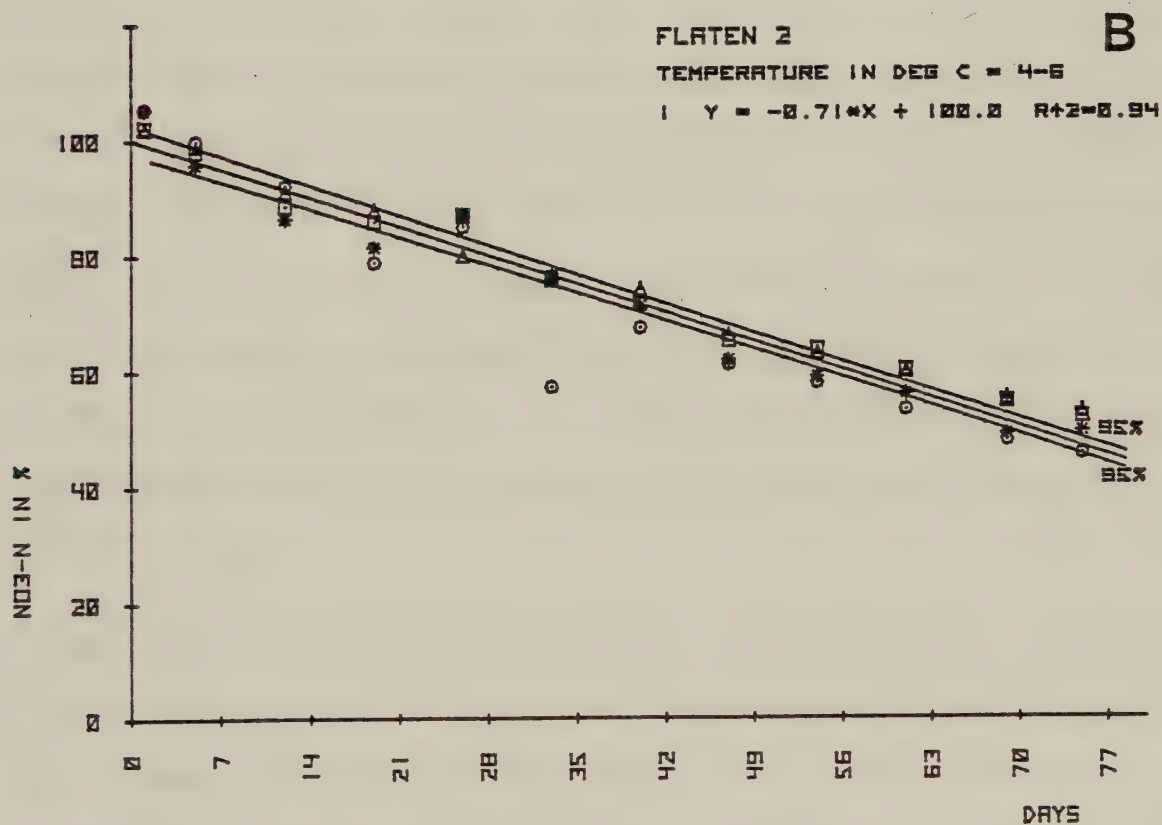
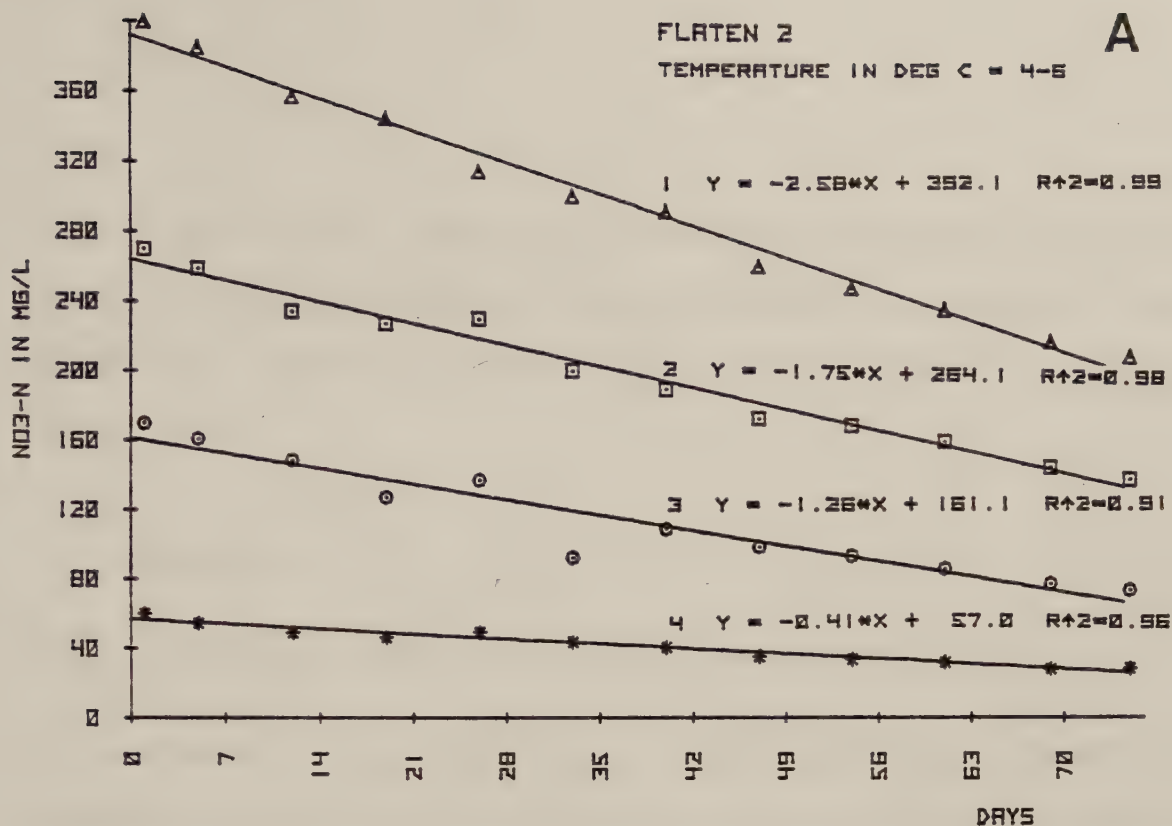


Fig 29) Experimental series Flaten 2. A) Nitrate concentrations in water above sediment incubated anaerobically at 4-6 °C. Symbols and regression lines: (Δ ,1) initial nitrate concentration 390 mg NO₃-N/l, ($\square$,2) 265 mg NO₃-N/l, ($\circ$,3) 160 mg NO₃-N/l, and ($\star$,4) 55 mg NO₃-N/l. B) Results expressed as % of initial nitrate concentrations. Regression line with 95 % confidence interval obtained from all data pooled.

entire experiment. After the treatment of Lake Lillesjön (when Ca-nitrate had been denitrified and pH values between 5 and 9 achieved) a survey showed that all three groups were present (cf. section 6).

3.4. Discussion

3.4.1. General characteristics of the sediment

The sediment survey showed that the highly-reducing sediment was restricted to the area of the lake basin with a water depth greater than 3 m. The water column over this area is stratified from the end of April to the end of September. The morphometry of the lake basin contributes to amplified hypolimnetic conditions due to a funnel effect (Ohle 1962) and stabilized the stratification.

With the exception of sodium, the chemical composition of the sediment was similar at the various water depths. The accumulation of sodium in the sediment at 4 m water depth was probably caused by the large amounts of degrading Lemna which were deposited annually in this area.

Alkalinity, ammonia and phosphate concentrations in the sediment interstitial water at different depths were highly interrelated and showed - except for phosphate at 4 m depth - constant molar ratios. This indicates a dynamic pool of dissolved matter (pool = steady state concentration) regulated by bacterial activity and by release, sorption and diffusion processes. Since the matrix of the sediment (analyses on a dry weight basis) is similar at all three

depths, the differences in dissolved matter seem to be related to the release rate determined by the intensity of bacterial processes, the environmental requirements of the bacterial populations and the structural properties of the sediment.

3.4.2. Oxygen demand

Oxygen demand is a measure of reduced inorganic species plus the potential rate of bacterial degradation of different organic species.

When oxygen demand measurements of the sediment at 2, 3 and 4 m water depth are compared, it is clear that anaerobic conditions have affected the oxygen uptake characteristics of the sediment at 4 m depth. A large amount of reduced inorganic species and easily degradable organic matter contribute to the high initial oxygen demand of this sediment.

The efficiency of bacterial populations with respect to net energy gain is lower under low redox conditions and more substrate must be supplied and metabolized by anaerobic bacteria than by aerobic bacterial populations. Energi is obtained under anaerobic conditions either by release of bonding energy through cleavage of organic molecules or by oxidation of organic substrate with CO_2 , SO_4 , NO_3 or NO_2 as terminal electron acceptor.

The oxygen demand studies and the studies of P release clearly indicated that the sediments of the deepest part of the basin were responsible for the high internal fertilization of Lake Lillesjön.

3.4.3. Phosphorus exchange in relation to bacterial communities

P exchange processes between sediment and water may be divided into two steps:

- 1) The release of P from sedimented material of biological origin and of P sorbed on inorganic compounds (Fe-, Al-complexes).
- 2) Transport to the lake water.

Release processes and equilibrium concentrations between sediment and the overlying water were studied in this work. Release of phosphorus and equilibrium concentrations are discussed in terms of bacterial populations and their spatial distribution in the sediment.

The difference between aerobic and anaerobic bacterial populations in terms of energy transfer efficiency was mentioned above. Differences in the spatial distribution of the bacteria can be anticipated (Oláh 1972, Jannasch & Pritchard 1972). Since each organism is dependent on substrate supply and the removal of metabolites (e.g. through diffusion), these requirements will control spatial distribution of bacterial populations according to the following 3 models:

- 1) The low energy gain of bacteria under low redox conditions necessitates high substrate concentrations and probably a high individual motility. The ratio between substrate and bacterial biomass will be high, and high concentrations of reduced metabolites will poise the environment at the low redox level required by the bacteria.

2) The requirements of aerobic heterotrophs in sediments are access to dissolved oxygen and organic matter. Most of the dissolved organic compounds are easily oxidized by molecular oxygen which is thus depleted. Only a structure consisting of particulate organic substrate with attached bacteria and large interstitial spaces low in dissolved organic matter allows oxygen transfer. This spatial distribution of bacteria, although common in aerated soils, is maintained only in oligotrophic lakes with a minimum of sedimenting organic material and good oxygen supply at the sediment surface.

3) The third possible structure is a combination of nitrifying (chemoautotrophs requiring oxygen and ammonia) and denitrifying bacteria (usually heterotrophs with the ability to use NO_2 or NO_3 as electron acceptors). Such communities consisting of attached denitrifying bacteria and free-living nitrifying bacteria show a good efficiency (c. 10 % lower than communities using O_2 as electron acceptor, but higher than e.g. sulphate-reducing bacteria, cf. Schlegel 1969). The terminal products are N_2 and CO_2 which are easily removed from the environment. The metabolic products of the nitrifying bacteria are utilized by denitrifying bacteria on particulate organic matter. A shortage of ammonia results in a surplus of oxygen thus altering the denitrification process into a heterotrophic process using O_2 as electron acceptor. This means that there is a self-regulating system at the sediment surface in which nitrogen metabolism is the key to oxygenation and nutrient cycling.

Ripl & Lindmark (1978 a) found in experiments with helium-flushed sediments from eutrophic lakes that most of the oxygen added stoichiometrically corresponded to evolved N_2 , if nitrite was considered to be the only intermediate. Completely mixed sediment systems, however, showed an increased utilization of oxygen for heterotrophic activities. Sediments from oligotrophic lakes showed less nitrification-denitrification and a larger heterotrophic oxygen demand.

If a heavy "rain" of fresh organic matter caused by e.g. a plankton outburst "loads" the sediment surface, sediment processes and the spatial distribution of bacterial populations in equilibrium with oxygen supply are changed. This affects both nitrification at the sediment water interface and denitrification on particulate organic matter. The bottom water is rapidly depleted of oxygen, NH_4 accumulates and the redox potential drops quickly due to the low redox buffer capacity of the water. An anaerobic situation is established.

Anoxic conditions in the hypolimnion of Lake Lillesjön were thus a result of:

- 1) an altered physical sediment structure due to permanent anoxic conditions in the sediment, and
- 2) the large amounts of fresh organic matter (Lemna minor) produced in the lake due to recycled nutrients. This stabilized the hypolimnetic environment at a low redox potential.

The distributions of sorbed, organic particulate, organic dissolved and phosphate phosphorus are intimately connected with redox

conditions. Since the work of Einsele (1936) and Mortimer (1941, 1942) on phosphorus release and sorption due to the oxidation state of iron and manganese compounds, many phosphorus exchange models have been proposed. Banoub (1976) related bacterial populations and activity to phosphorus release from sediments.

Most of the experiments in the present study were conducted under anaerobic conditions. Large differences in P concentrations and P outflow from the sediments were obtained depending on the type of chemicals added. Nitrate-treated sediments and sediments from 2 and 3 m water depth in Lake Lillesjön released considerably less phosphorus than sediments taken at 4 m depth and incubated without NO_3 addition.

The effect of NO_3 addition on P outflow from the sediment was probably through oxidation of iron compounds (the reduction of NO_3 to N_2 occurs at a higher redox level than the reduction of ferric to ferrous iron). The attached denitrifying bacteria in the sediment were, however, maintained at low interstitial concentrations of dissolved phosphate. Although the apparent phosphate concentration in the interstitial water was low, extremely high denitrification rates were observed. Obviously, the turnover rate of phosphorus was also high. A short-circuited phosphorus transport within the microhabitat of the attached bacteria is assumed.

The sediments from 2 and 3 m depth still had oxidized iron compounds available and contained less oxygen-demanding organic matter. This prevented a drop in redox potential which would have

favoured the development of the strictly anaerobic bacteria described above.

It seems, therefore, that the release of P from sediment is more a function of sediment micro structure, including bacteria, than a matter of anaerobic versus aerobic conditions. This is further supported by the results of experiments in which iron was added to the sediment. According to the solubility product, the precipitation of ferric iron in the sediment should have depressed P concentrations in the interstitial water to extremely low levels. Lowered denitrification activity would have been expected due to P shortage in the interstitial environment. Neither of these expectations were realized.

Only nitrate additions influenced the exchange of P between sediment and water. Additions of lime and iron were not necessary to decrease the outflow of P from the sediment. A second, one-month incubation of nitrate-treated cores at room temperature after the nitrate from the initial addition had been depleted resulted in low phosphate levels. Phosphate concentrations in the water above the sediment stabilized at a level about twice that found when nitrate was present, but considerably lower than before nitrate treatment.

3.4.4. Denitrification kinetics

The problems involved in the measurement of denitrification in water-sediment systems are associated with experimental design. The measurement of nitrate (or the sum of nitrate and nitrite) in

the water phase above the sediment as a measure of denitrification offers the advantage of simplicity.

However, several conditions must be fulfilled if the decrease in nitrate is to be taken as a measure of denitrification.

- 1) It must be shown that practically all nitrate is converted to molecular nitrogen.
- 2) The denitrification rate in the sediment must be proportional to the decrease in nitrate in the water above.

In experiments with various sediment types, it was shown that the conversion efficiency of NO_3 to N_2 was in all cases above 90 % when high concentrations of NO_3 (5 mg $\text{NO}_3\text{-N/l}$) were applied. Similar results were obtained by van Kessel (1967).

The spatial distribution of the denitrifying bacterial populations was shown by the kinetics of denitrification in the core experiments. With the high nitrate concentrations used in these experiments (50 - 1000 mg $\text{NO}_3\text{-N/l}$), zero-order denitrification kinetics were observed.

van Kessel (1976) obtained first-order kinetics at low NO_3 concentrations and zero-order kinetics with increasing nitrate concentrations (i.e. nitrate removal became independent of concentration). However, in his experiments highly minerogenic sediments were used (water content 25-30 % and organic matter 2-3 % of dry matter).

Harremoes (1975) showed 0.5-order kinetics for denitrification filters in sewage treatment plants due to "partly effective"

filter pores. In these denitrification filters the bacterial populations are attached, but in contrast to sediments, the organic substrate is available as methanol.

In the experiments of the present study, linear depletion of nitrate with time (zero-order kinetics) is possible only with an attached population of denitrifying bacteria in the interstitial space on a non-limiting organic particulate substrate. However, as demonstrated in Lake Lillesjön experiment series 5 (cf. Fig 25 A), first-order kinetics were approached when nitrate concentrations decreased below 10 mg N/l.

An unexpected feature of the "undisturbed" core systems was the dependence of denitrification rates on initial NO_3 concentrations. However, calculated as a percentage of the initial nitrate concentration, denitrification rates were similar for different initial nitrate levels. Different denitrification rates were observed for sediments with different properties.

A plot of denitrification rates in mg $\text{NO}_3\text{-N/l.d}$ against initial nitrate concentrations (intersect of regression line with the ordinate) showed a nonlinear relationship (Fig 30).

The differences between Lake Lillesjön and Lake Flaten sediments on the one hand and the sediments of several Stockholm lakes on the other were mainly in water and clay content. Nonlinearity in the relation between initial nitrate concentrations and denitrification might indicate interactions of the strong electrolyte calciumnitrate with the sediment resulting in coagulation effects,

DENITRIFICATION IN SEDIMENTS

1 $Y = -0.515 \cdot \text{EXP } X \cdot 4.43E-3 \quad R^2 = 0.88$

2 $Y = -0.454 \cdot \text{EXP } X \cdot 3.24E-3 \quad R^2 = 0.67$

+ = LILLESJÖEN ○ = SHLM ST

* = FLATEN

DENITRIFICATION IN MG N / L * DRY

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dewatering of lyophilic colloids and increased interstitial space.

It should be noted that extrapolation of the results in Fig. 30 would lead to absurd consequences. Decreasing denitrification rates are expected if nitrate concentrations are further increased.

The dependence of denitrification rates on temperature was found to be similar to that reported by van Kessel (1976), i.e. a value of 6 %/ °C in the interval 5 to 23 °C. This is close to Q_{10} values reported for heterotrophic oxygen uptake in sediment cores (Granéli 1977 b).

4. Lake Lillesjön

4.1. Physiographic description

Lake Lillesjön is situated in the south Swedish uplands ($57^{\circ} 10'N$, $13^{\circ}56'E$), about 7 km west of the town Värnamo in the county of Jönköping, 166 m above sea level. The lake is fed by seepage from a watershed of about 1 km^2 . The drainage is estimated to about 10 l/s, which gives a theoretical water renewal time of about 3 months. However, the protected location of the lake together with precipitation and drainage patterns usually result in incomplete water exchange and high stability of stratified conditions.

Geologically, the area is formed of igneous rocks and moraine to the east and south, while peat bogs are situated close to the northern and northwestern shores. The vegetation cover of the drainage area is characterized by coniferous forest, scrub and bushes.

Close to the western shore there is a small village, Kärda, with about 300 inhabitants. To the southeast, close to the shore, a treatment plant for ground water supplies the village with drinking water.

A map of Lake Lillesjön is shown in Fig 6 and a hypsographic diagram in Fig 31. Morphometric data for Lake Lillesjön are the following:

Area	$42\,000 \text{ m}^2$
Volume	$86\,000 \text{ m}^3$

LAKE LILLESJÖN

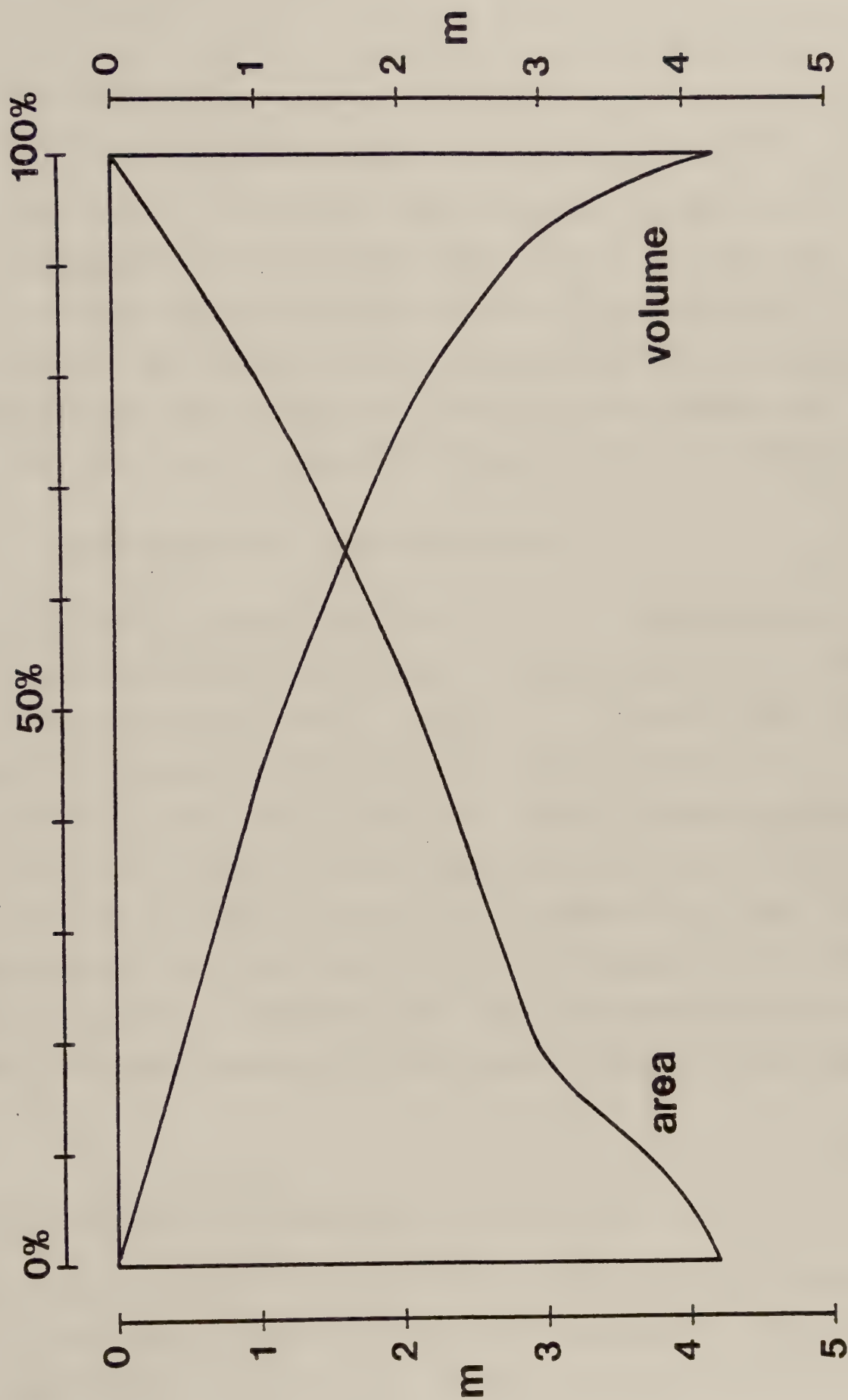


Fig 31) Hypsographic curves for Lake Lillesjön.

Maximum depth	4.2 m
Mean depth	2.0 m

The mean annual precipitation (over 30 years) is 698 mm and mean temperature 6.5 °C. During 1975, the year when the lake was restored, precipitation was extremely low (584 mm) and temperature relatively high (8.0 °C) (data from SMHI (Sveriges Meteorologiska och Hydrologiska Institut) annual reports for the town of Ljungby, situated c. 35 km south of Lake Lillesjön).

4.2. Lake Lillesjön as a sewage receiver

Lake Lillesjön, a small lake which lacks all characteristics of a suitable recipient, was used as a receiver for at most mechanically treated sewage during a period of c. 15 years until 1971. Granéli & Leonardson (1973) estimated the annual load of phosphorus to about 300 kg, while the natural phosphorus supply was estimated to about 10 kg/a. Deposition of phosphorus in the sediment of the lake was low and was estimated to at most 10 % of the annual load. The upper 15 cm of the sediment contained about 15 g P/m², a relatively low value when compared to sediments from other receivers in this region (Granéli & Leonardson op. cit.).

4.3. Lake Lillesjön after sewage diversion

In 1971 all sewage was diverted from Lake Lillesjön and pumped to a modern sewage treatment plant. The remaining P load in drainage water was close to the natural background (10 kg/a). However, when the lake was thoroughly investigated in 1972,

no improvements could be noted. On the contrary, expanding macrophyte vegetation, extremely high nutrient recycling from the sediment, practically anoxic conditions in the whole water column ($0.7 \text{ mg } O_2/l$ at 0.2 m), and a dense cover of duckweed (Lemna minor) during summer characterized the lake ecosystem. Interstitial water nutrient concentrations were extremely high ($PO_4\text{-P}$ $8\text{-}10 \text{ mg/l}$, $NH_4\text{-N}$ $39\text{-}58 \text{ mg/l}$), and in anaerobic nutrient exchange experiments, $PO_4\text{-P}$ concentrations in water above the sediment reached $10\text{-}17 \text{ mg/l}$. The range of P concentrations in the epilimnion was $0.4\text{-}2.3 \text{ mg/l}$ and in the hypolimnion $0.8\text{-}5.5 \text{ mg/l}$. $NH_4\text{-N}$ accumulated in the hypolimnion to concentrations of about 20 mg/l . Due to the high organic load most of the sulphate in the hypolimnion was depleted, and only $2 \text{ mg/l } SO_4$ was found at 3.5 m after summer stagnation from an initial concentration of 15 mg/l . Enrichment of the hypolimnion water with sodium and potassium by factors of 1.7 and 2 , respectively, indicated the strong influence of decaying Lemna. The oxygen demand of sediment taken at 4 meter depth is given in Fig 32 (data from Granéli & Leonardson 1973).

More or less intact lakes of this region are characterized by oligotrophic conditions. Lake Lillesjön, heavily polluted by sewage effluents, had changed to a highly eutrophic or hypertrophic lake ecosystem. In 1977 43% of the lake was colonized by emergent and floating-leaved plants. Floating-leaved plants had colonized the lake bottom down to a depth of a c. 2 m . Nyphar luteum and Nymphaea alba were dominant, but Potamogeton natans and Polygonum amphibium also occurred in large quantities. Typha latifolia, Calla palustris and Carex rostrata had colonized

LAKE LILLESJÖN

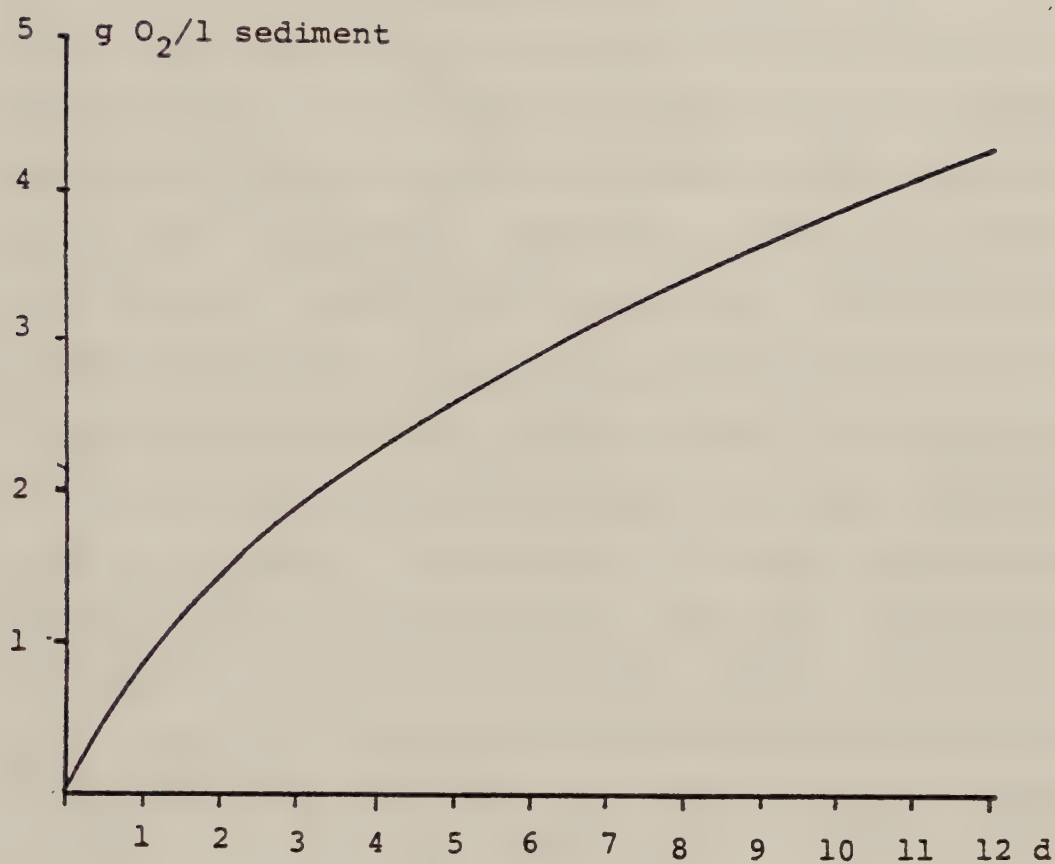


Fig 32) Oxygen demand (obtained with Sapromat at 20°C) of Lake Lillesjön sediment taken at 4 m water depth during autumn 1972, i.e. one year after diversion of sewage from Lake Lillesjön. (From Granéli & Leonardson 1973)

the shallow western shore. Due to vigorous gas development in the sediment, plaur formation occurred. The remaining lake area (57 %) was covered by Lemna minor during summer. Underwater light intensities were highly reduced during this period and often insufficient for the development of phytoplankton, thus favouring an almost exclusively heterotrophic community in the water mass. Zooplankton occurred in a thin layer close to the water surface, where oxygen was present in low concentrations. A mass development of Daphnia pulex was recorded in autumn 1972. On one sampling occasion in spring 1972 a phytoplankton bloom was recorded. Silica concentrations had then decreased to less than 0.1 mg SiO₂/l, and inorganic nitrogen compounds were almost totally depleted. In summer and autumn the submersed parts of the macrophytes were covered with a dense "Aufwuchs" of Sphaerotilus natans. An exhaustive description of conditions in Lake Lillesjön during 1972, one year after diversion of sewage, is given by Granéli & Leonardson 1973).

5. Restoration equipment, restoration measures and monitoring program for the denitrification phase.

5.1. Restoration equipment

A special apparatus was developed for application of the chemicals to the sediment. Aeration devices have been described by Mercier (1949), Bernhardt & Hötter (1967), Fast (1971), Bengtsson et al. (1972), and Ohle (1972, 1975), but the apparatuses used were stationary and were used to aerate anoxic hypolimnetic water. Björk (1968) and Ohle (op. cit.) proposed the addition of chemicals for phosphate sorption or precipitation in connection with aeration, e.g. through a Limno apparatus developed by Atlas Copco.

For sediment treatment in situ, the application device had to meet the following criteria:

- 1) Chemicals should be applied evenly and directly to the sediment without risking excessive concentrations of chemicals in the water column.
- 2) The sediment should be gently stirred before application of the chemicals, thus activating the sediment and providing thorough mixing of the chemicals with the re-sedimenting particles.
- 3) The treatment time for the total area (1.2 ha) should be kept within reasonable limits (less than a week).
- 4) Small obstacles at the sediment surface should not damage the device or delay operation.
- 5) The device should be easy to move both horizontally and vertically.

The restoration device, an air-operated harrow, was designed in cooperation with the Atlas Copco Central Laboratory for Physics, Stockholm, and a prototype was built (Fig 33). The harrow consisted of three frames 100 x 200 cm, built in 1 inch steel tubing and equipped with 3 rows of evenly-spaced nozzles. The nozzles were 30 cm long and protruded 5 to 10 cm into the sediment. The rows were placed 7 cm apart and stirred the sediment thoroughly with air bubbles every 7th cm over a distance of 6 meters. The nozzles were mounted on the steel frames with rubber connections which allowed some flexibility. The segments were chained to a tiebeam and connected to a towing wire. At the rear of the segments a plastic tube with the chemical injectors was mounted. Each segment was equipped with 8 injectors spaced 20 cm apart. Due to the aggressiveness of the iron chloride solution, acid-resistant material had to be chosen for the injector parts, tubing connections and pump (Picture 1).

5.2. Treatment design and quantification of chemicals

The sediment was pretreated with iron chloride (FeCl_3) and neutralized with slaked lime ($\text{Ca}(\text{OH})_2$) before the nitrate addition. A suitable dosage of 146 g Fe/m^2 was determined from results of laboratory experiments. This increased the Fe content of sediment dry matter with about 15 mg/g over a depth of 20 cm. The purpose of the iron addition was to increase the P sorption capacity and the redox buffer capacity in the sediment. The lime dosage was calculated to 180 g Ca/m^2 as $\text{Ca}(\text{OH})_2$ for neutralization of the protons liberated by the iron addition.

Due to the acidification with iron chloride in connection with aeration, H_2S was removed from sediment in experimental systems.

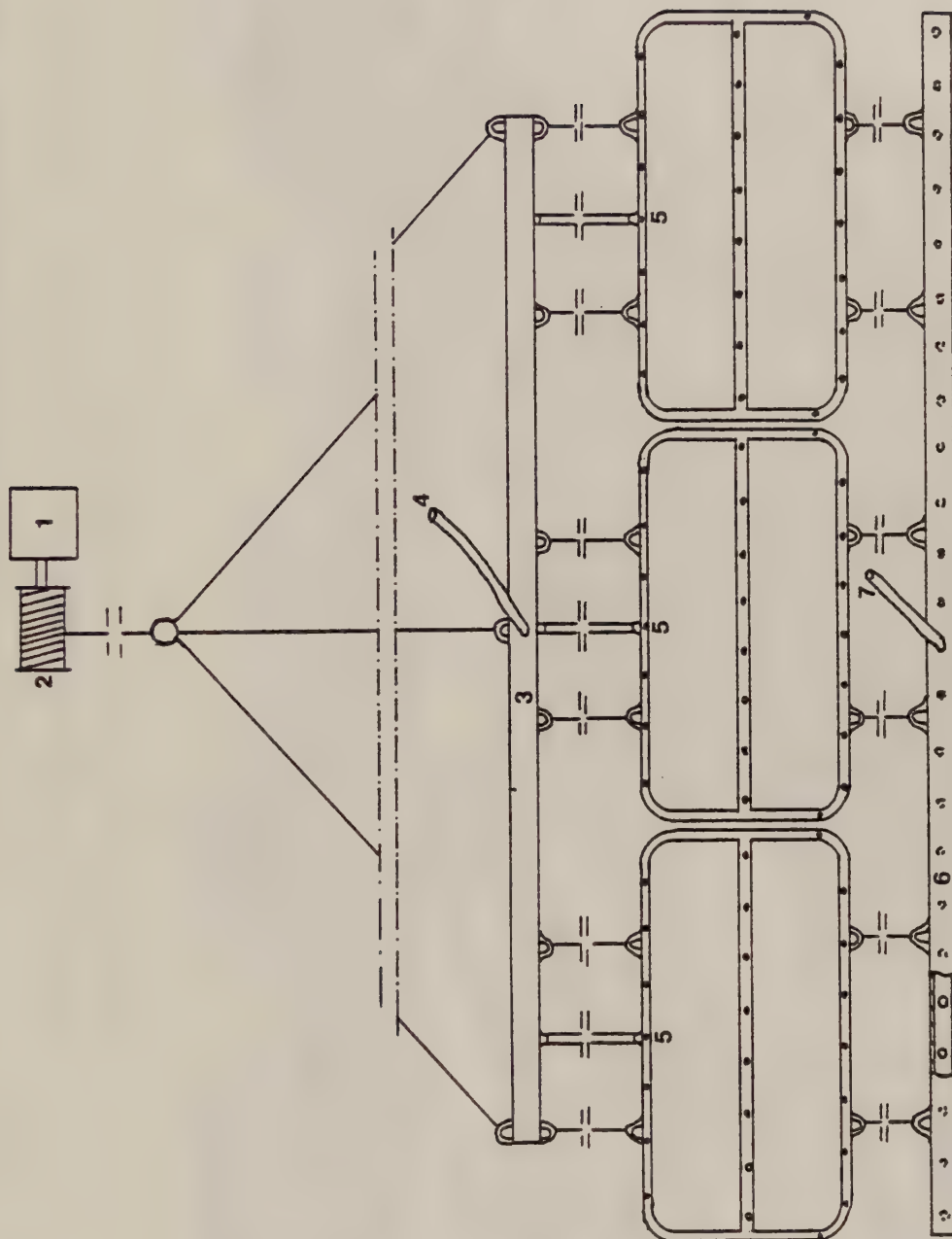


Fig 33) Apparatus for application of the chemicals to Lake Lillesjön sediment. Sediment harrow prototype built by Atlas Copco Central Laboratory for Physics, Stockholm. 1) Pneumatic motor 2) Cable winch 3) Tie-beam 4) Air inlet 5) Aeration segments with air inlet and nozzles 6) Injector for chemicals with injector nozzles 7) Inlet for chemical solutions.

Picture 1) Sediment harrow and container for the chemicals in front of
Lake Lillesjön (Foto Hans Berggren).



This corresponded to a reduction of the oxygen demand by about 0.5-0.7 g O₂/l sediment.

The short-term oxygen demand of the upper sediment layers was estimated to about 3.5 to 4.0 g O₂/l sediment, and the instant chemical and biological oxygen demand on a m² basis to between 400 and 500 g O₂. Therefore an application per m² of 480 g O₂ chemically bound to 141 g N was indicated (= 1 kg technical Ca-nitrate/m²). Technical water-soluble calcium nitrate, Ca(NO₃)₂·4H₂O, was chosen as oxidation agent. This was same chemical used in laboratory experiments.

The effects of nitrate treatment on sediment oxygen demand at 4 m depth were demonstrated in laboratory experiments (Sapromat) conducted with sediment from series Lillesjön 2 (cf. Fig 13). The effects of the treatment on interstitial water and sediment structure proved satisfactory (cf. Fig 22 B).

The depth of treatment in the sediment was determined by the thickness of the sulphide-containing layer. As demonstrated in oxygen demand experiments (Sapromat), this black, top sediment had about twice the oxygen demand of the underlying sediment.

Sediment oxidation experiments further showed that treatment of the upper 10 cm was sufficient for a long-term improvement of the sediment with respect to oxygen uptake and phosphorus liberation. This was shown with nitrate-treated sediment incubated at room temperature for several months.

Suitable primary dilution ratios for the chemicals were also estimated in tests with laboratory cores. Dilution on a weight

basis of 1 to 10 with water gave working solutions which, when applied at the sediment surface, diffused to 10 to 15 cm. This dilution gave maximum nitrate concentrations in the environment of between 500 and 1000 mg N/l.

Treatment of a central area 1.2 ha in Lake Lillesjön was estimated to be sufficient to cover all sediment requiring restoration.

A temperature coefficient of 6 %/ $^{\circ}\text{C}$ in the interval 5-23 $^{\circ}\text{C}$ was estimated for the denitrification process, corresponding to a doubled reaction speed when temperature is increased 12 $^{\circ}\text{C}$.

The combined iron and slaked lime addition showed a positive effect on denitrification and increased the rate with about 20 %.

From the monitoring programme the duration of summer stagnation was known to be from the end of April until the end of September. The treatment was therefore planned for May. Temperatures between 8 and 16 $^{\circ}\text{C}$ were expected, and it was calculated that denitrification of all nitrate added would require about 60 days.

5.3. Application of the chemicals

The sediment was treated between April 16 and May 21, 1975, according to the following time schedule:

16 Apr	-	22 Apr		Installation of the equipment
23 Apr	-	6 May		Application of FeCl_3 solution
7 May	-	14 May		Application of slaked lime
17 May	-	21 May		Application of Ca-nitrate

A corrosion-resistant mixing container with a capacity of 15 m^3 was installed on the shore. Two pumps were used, one for pumping lake water to the mixing container (capacity 110 l/min), and one corrosion-resistant pump (capacity $2 \times 300 \text{ l/h}$) for distribution of the chemicals. All equipment was rented from EKA Bohus Electrochemical Company, the suppliers of FeCl_3 . A compressor (Atlas Copco Super Silence Air WSS 250, capacity $7.1 \text{ m}^3/\text{min}$) was installed for 1) mixing the chemicals in the mixing tank by air injection, 2) pulling the harrow and 3) stirring the sediment. Buoys were installed in the lake to mark the area to be treated and to align the movement of the harrow. A pneumatic winch was used for pulling the harrow in one direction. The harrow was then lifted to the surface with floats and towed back to the starting line (marked with buoys) by a boat equipped with a 7 kW outboard motor. A schematic view of the installation is given in Fig 34.

One treatment of the area (1.2 ha, $90 \times 133 \text{ m}$) required 3 to 4 days using 14-15 transects 133 m long and 6 m wide (the width of the harrow). The treatment of one transect required c. 1 h, and the speed of the harrow on the sediment surface was about 2 m/min. The chemicals were diluted 1:10 by weight in the mixing container before application and processed in 14 batches per treatment.

The chemicals were mixed by air injection at the bottom of the mixing container. The dosage of the chemicals was manually controlled. The mixed chemicals were thereafter injected directly at the sediment surface.

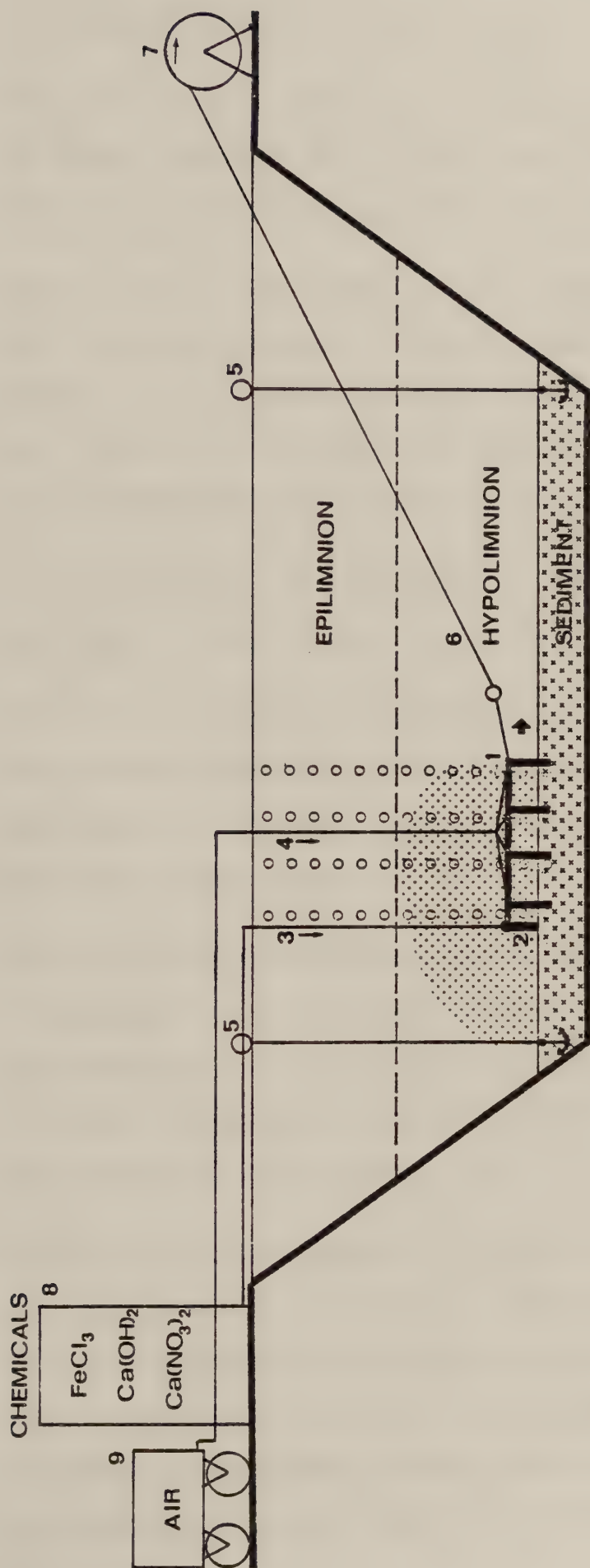


Fig 34) Schematic diagram of the sediment treatment equipment used in Lake Lillesjön. 1) Sediment harrow 2) Injector nozzles for chemicals 3) Supply tubing for chemicals 4) Supply tubing for air 5) Buoys 6) Towing line 7) Cable winch 8) Mixing container with pump for chemicals 9) Air compressor.

5.4. Monitoring the restoration measures

Addition of the chemicals was monitored by analyses performed on water, sediment and interstitial water. Plankton samples were taken in connection with water samples.

Water analyses were compiled in time-depth diagrams before and after restoration (cf. 6.1.). Changes in plankton composition are discussed in section 6.3. In this chapter the direct effects of the addition of chemicals on the water column and on sediment composition are described.

The distribution of chemicals by the harrow was monitored for evenness of application and vertical distribution.

After the addition of iron to the sediment, the water column also showed decreased pH values. While pH 7.0 was recorded in the water at 1 m depth, the pH values at 2 and 4 m were 4.0 and 3.2, respectively.

Iron concentrations in lake water were 3.9 mg Fe/l at 2 m depth, 21.1 mg Fe/l 4 m depth and 35 mg Fe/l at the sediment-water interface. Of the total amount iron added (1759 kg), only 18 % (320 kg) was found in the water mass, while 82 % was directly distributed to the sediment.

Although the distribution of iron over the treated area was satisfactory, analyses of sediment cores showed a rapid diffusion downwards, probably due to the density of the iron solution. When slaked lime was thereafter injected into the sediment, the iron solution had already sunk to depths not reached by the alkaline solution. Thus only slight enrichment of the

upper sediment layers with Fe was achieved on a dry matter basis. However, the iron concentrations found in the interstitial water and the outflow of iron from the sediment at the deepest part of the lake were sufficient to precipitate the phosphate accumulated during stagnation periods.

The addition of lime caused an immediate precipitation of 63 % of the residual iron in the water column, and after c. 1 month iron reached concentrations of 0.1-0.2 mg Fe/l.

The neutralizing effect of the lime addition on the water column was most satisfactory. The immediate effect was to raise pH values to between 7.8 and 10.2. Within one week pH dropped to between 7.1 and 9.4. Alkalinity and buffer intensity were thereby reestablished in the water column. The added calcium accumulated in the upper sediment layers together with the calcium added by the Ca-nitrate addition (cf. Fig 21).

Ca saturation with respect to equilibrium with the carbonic acid system increased from saturation values obtained on April 18 to supersaturation (c. 500-600 %) on May 20, but reached saturation conditions again on May 27. A low carbon dioxide tension ($p\text{CO}_2 = 4-5$) induced by the addition of slaked lime contributed to the rapid normalization of the water with respect to ionic composition and pH.

The addition of Ca-nitrate was monitored by taking 14 sediment Cores at random over the entire treated area. Samples for nitrate analysis were taken from the water above the sediment cores. The mean concentration in these samples was 43.7 mg $\text{NO}_3\text{-N/l}$

with a standard deviation (s) of 17 mg N/l. Ammonia (c. 1 % impurity in the Ca-nitrate added) was distributed similiary with a mean of 59 mg N/l and $s = 18 \text{ mg/l}$. pH varied in the samples between 7.0 and 7.6. The mean conductivity value in this near-bottom water was $300 \mu\text{S}_{20}/\text{cm}$ with $s = 77 \mu\text{S}_{20}/\text{cm}$ after the addition of nitrate. Conductivity in water sampled at 4 meters during summer stagnation before treatment was about $340 \mu\text{S}_{20}/\text{cm}$ (Aug 16 1974).

The denitrification of the added nitrate was followed by measuring nitrate distribution at two sampling stations in the water and in the interstitial water down to a depth of 30 cm.

The results (Fig 35) show the rapidity of the denitrification process in the sediment. The linearity of the process found in laboratory experiments was also confirmed. On the 1700 kg N added to the treated area, 620 kg were detected in the water mass while 1080 kg $\text{NO}_3\text{-N}$ (64 %) were directly delivered to the sediment.

65 % of the chemicals were therefore added to a sediment volume equal to 3 % of the volume of the water mass. A ratio between the concentrations of the chemicals in water and sediment, respectively, of 1:66 was obtained, which indicated the efficiency of the harrow in distributing chemicals without inter-mixing with the water column.

Denitrification activity during the first month was $3.2 \text{ g N/m}^2\cdot\text{day}$ which was equivalent to an oxygen uptake of $10 \text{ g O}_2/\text{m}^2\cdot\text{day}$. The N_2 evolved was estimated to c. $5 \text{ liters/m}^2\cdot\text{day}$.

LAKE LILLESJÖN NO₃-N mg/l

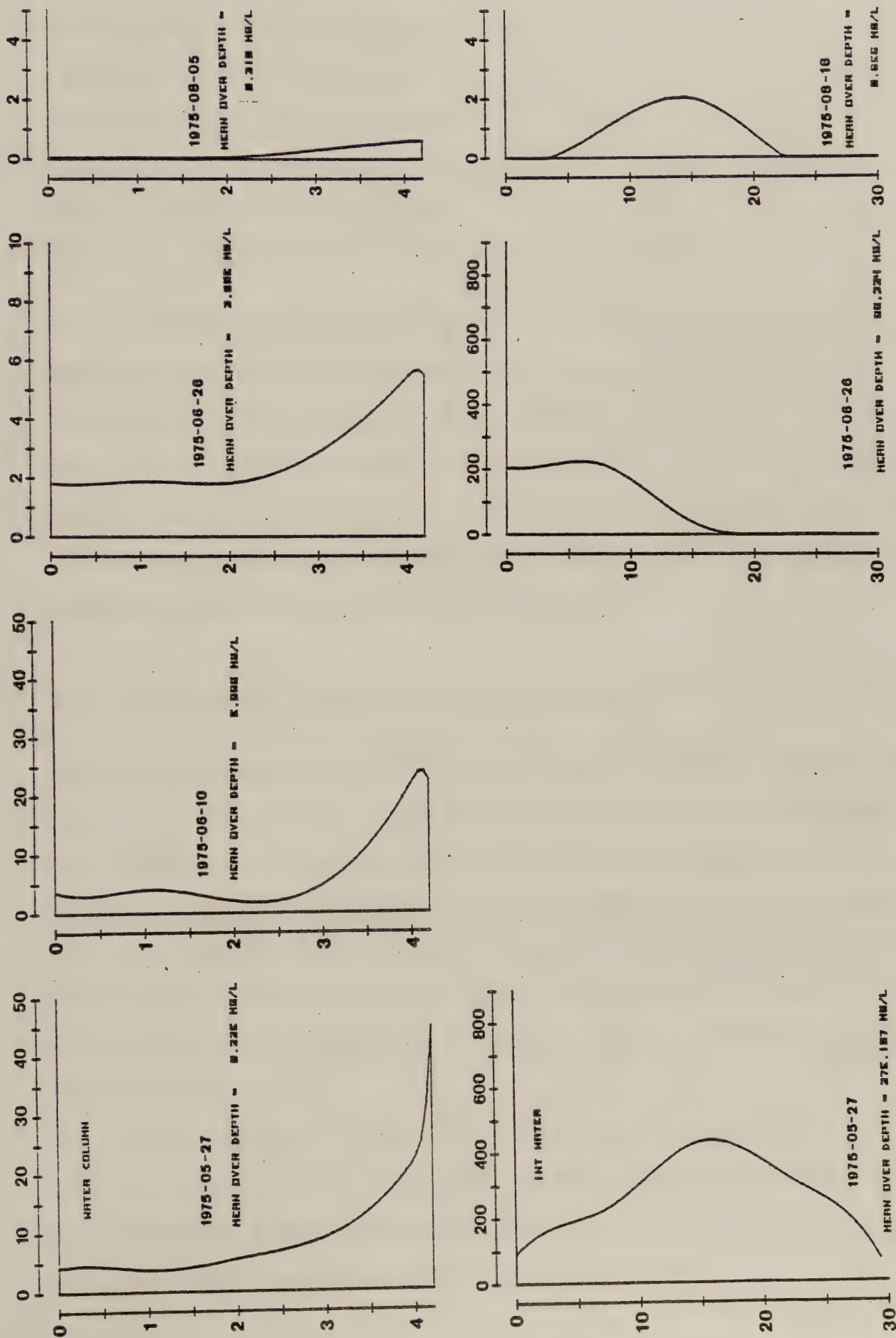


Fig 35) Distribution of nitrate in the water column and in the sediment interstitial water on various sampling occasions after addition of nitrate to Lake Lillesjön sediment. Curves are fitted by Cubic Spline functions.

After 37 days, 74 % of the added nitrate was denitrified, which gives a denitrification rate of c. 2 %/day. The vigorous evolution of gas from the sediments, caused in part by exceptionally high summer temperatures, resulted in a certain mixing of the stratified water mass (cf. Fig 36). Denitrification was therefore faster in the full-scale field treatment than predicted from laboratory experiments.

Due to addition of the chemicals and stirring of the superficial sediment by the harrow, the structure of the sediment was significantly changed. Sedimentation properties of sediment from previously anoxic zones (3-4 m) were changed from poorly sedimenting colloidal matter with resedimentation times of 4-5 hours to rapid sedimenting, larger particles with resedimentation times of only 10-20 minutes.

5.5. Treatment of the macrophyte vegetation

A severe consequence of the heavy sewage discharge during the receiver period of the lake was the rapid expansion of emergent graminids, nympheids and other aquatic plants, such as Calla palustris, Potamogeton and Polygonum species. 43 % of the lake surface was covered by rooted water plants when the restoration measures were planned. A large part of the remaining area was covered by a dense layer of duckweed (Lemna) during summer.

The annual loading to the lake of macrophyte detritus was estimated to at least 150 tons fresh weight (estimation based on standing crop figures during summer and on material harvested from the lake during the vegetation treatment).

These circumstances contributed, among other factors, to prevent recovery of the lake after sewage diversion. Together with restoration of the sediment, a partial elimination of macrophytes including root extraction was planned.

These measures were undertaken during August 1975 after the sediment treatment. The vegetation in an area of 1.8 ha was removed, and only a small reed area in the northern part of the lake was spared as nesting place for water fowl (cf. Fig 6). Eighty-three tons of macrophyte biomass (fresh weight) was removed with a pontoon-equipped mowing machine especially constructed for the removal of aquatic macrophyte vegetation (Björk 1968). Thereafter the root felt was cut by a rotocultivator. The floating rhizome and root pieces were removed from the lake.

These measures caused a temporary increase in phosphorus, ammonia and silica concentrations in the water and decreased oxygen concentrations. However, macrophyte removal was completed in one week, and the negative effects rapidly disappeared. Sediment samples showed that the vegetation treatment had no permanent adverse effects on the sediment.

6. The response of the ecosystem

6.1. Introduction

Since the end of April 1974, the water and sediment have been investigated during two periods:

- 1) a period of intensive investigation which started in April 1974 and proceeded until the end of June 1976, and
- 2) a period with reduced sampling frequency (4 times a year) from 1977 onwards.

This second period is planned to continue until 1980. Studies of the phytoplankton and two surveys of zoobenthos and fish have been carried out in connection with sampling for water chemistry.

6.2. The water

6.2.1. Temperature

Despite the limited depth (4.2 m), Lake Lillesjön is usually thermally stratified during summer (from May until September) and during winter if there is ice cover.

Due to the protected location, the onset of summer thermal stratification occurs almost immediately after ice break-up. The thermocline usually has an upper limit at about 2.5 m depth and is only slightly lowered during summer, although temperatures at the bottom rise to about 13-14 °C. The position of the thermocline is to a large extent influenced by the morphology

LAKE LILLESJÖEN TEMPERATURE DEG C

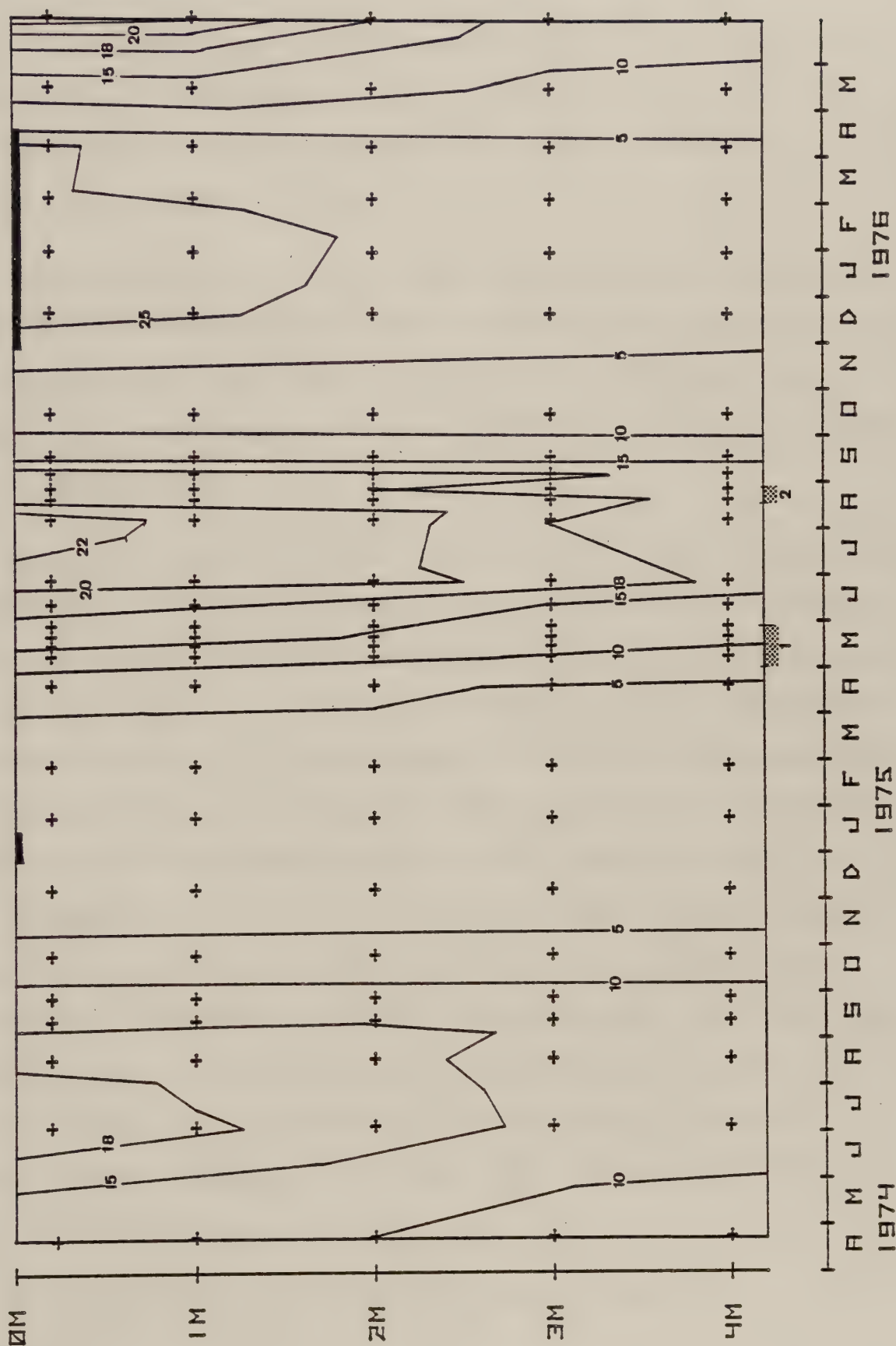


Fig 36) Time depth diagram for temperature in Lake Lillesjön. Solid line at top denotes ice cover. Dotted are- as at bottom indicate restoration measures; 1 = application of chemicals, 2 = removal of macrophytes.

of the lake. The funnel-shaped zone from 3 m to the maximum depth of 4.2 m comprises only 6-7 % of the total volume. The volume of the hypolimnion (below 2.5 m) is 13 000 m³ or 15.2 % of the total volume (86 000 m³).

The thermal properties of the lake allow the stable chemical stratification. The upper limit of the hypolimnion extends into the euphotic zone and large amounts of nutrients can thus be assimilated in primary production processes in the upper layer of the hypolimnion.

The mean air temperature for 1975 was 1.5 °C higher than the 30-year mean. Ice cover during winter 1974/1975 was extremely short (14 days), and no winter stratification was established. Summer temperatures in 1975 were extreme, and a maximum water temperature of 23.4 °C was measured in August. The temperature distribution in Lake Lillesjön during summer 1975 was affected by the nitrate treatment due to vigorous development of gas in the sediment (5 l/day) which mixed the water column. A mean temperature of 22 °C for the epilimnion and a weighted mean temperature of almost 19 °C in the hypolimnion were observed in August 1975. Sediment surface temperatures of about 17 °C during summer 1975 accelerated denitrification processes after nitrate addition to a faster rate than originally calculated (Fig 36).

6.2.2. Transparency, turbidity and water colour

While transparency and turbidity usually are related to the

presence of sestonic, light-scattering material, water colour is related to dissolved coloured humic substances. The magnitudes of these three parameters determine the light climate in the water column. However, the abundance of Lemna during summer 1974 resulted in a highly variable light climate, and sestonic particles had only minor influence.

Large particles, as for example zooplankton and large phytoplankton such as volvocales (Volvox aureus was found in considerable quantities after restoration, cf. section 6.3.), do not reduce transparency to low values (i.e. 50 cm), and their light-scattering ability is relatively small. Transparency after restoration varied between 159 and 250 cm with the exception of two occasions when transparency exceeded the maximum depth. This occurred when the sediment treatment was terminated but before vigorous gas development reduced transparency by re-suspending sediment (Fig 54).

Before restoration, high turbidity usually indicated a high abundance of bacteria in both the epi- and hypolimnion. Maximum turbidity in the entire water column was observed at the end of summer stagnation 1974 when values of 10-12 JTU were recorded in all water samples. This high turbidity occurred during the mixing phase when large amounts of ammonia and other reduced inorganic compounds were oxidized. After restoration turbidity varied between 0.8 and 6.5 JTU with a median value of about 2 JTU, and the highest values were observed in the metalimnion. Extremely high values above the sediment

surface were artefacts due to aeration of anoxic waters and precipitation of iron compounds or elemental sulphur (samples became turbid during transport to the laboratory).

Before restoration water colour was about 50-60 mg Pt/l. After restoration this was reduced to 15-40 mg Pt/l with a higher values in connection with heavy seepage from the surroundings during autumn and spring. With respect to water colour Lake Lillesjön can be classified as mesohumic.

6.2.3. pH and the carbonic acid system

Water in Lake Lillesjön is usually neutral, and pH values vary between 6.5 and 7.5. However, on occasions with heavy phytoplankton development maximum pH values of 9.7 were observed. Lake Lillesjön had well-buffered water before restoration with a mean alkalinity of c. 0.6-0.7 meq/l. Alkalinity varied between 0.35 and 2.4 meq/l with the highest values during summer 1974 in the lower hypolimnion when decomposition was at a maximum. Inorganic carbon concentrations were evaluated from alkalinity and pH. In figures 37 and 38 time-depth diagrams of pH and alkalinity are shown.

The water was supersaturated with carbon dioxide with respect to atmospheric equilibrium during almost the entire investigation. This indicated a dominance of heterotrophic processes in the water column. Before restoration a large increase in inorganic carbon was registered in the hypolimnion. During 44 days in July to August 1974, $380 \text{ mg C/m}^2 \cdot \text{d}$ were released.

LAKE LILLESJOEN PH UNITS

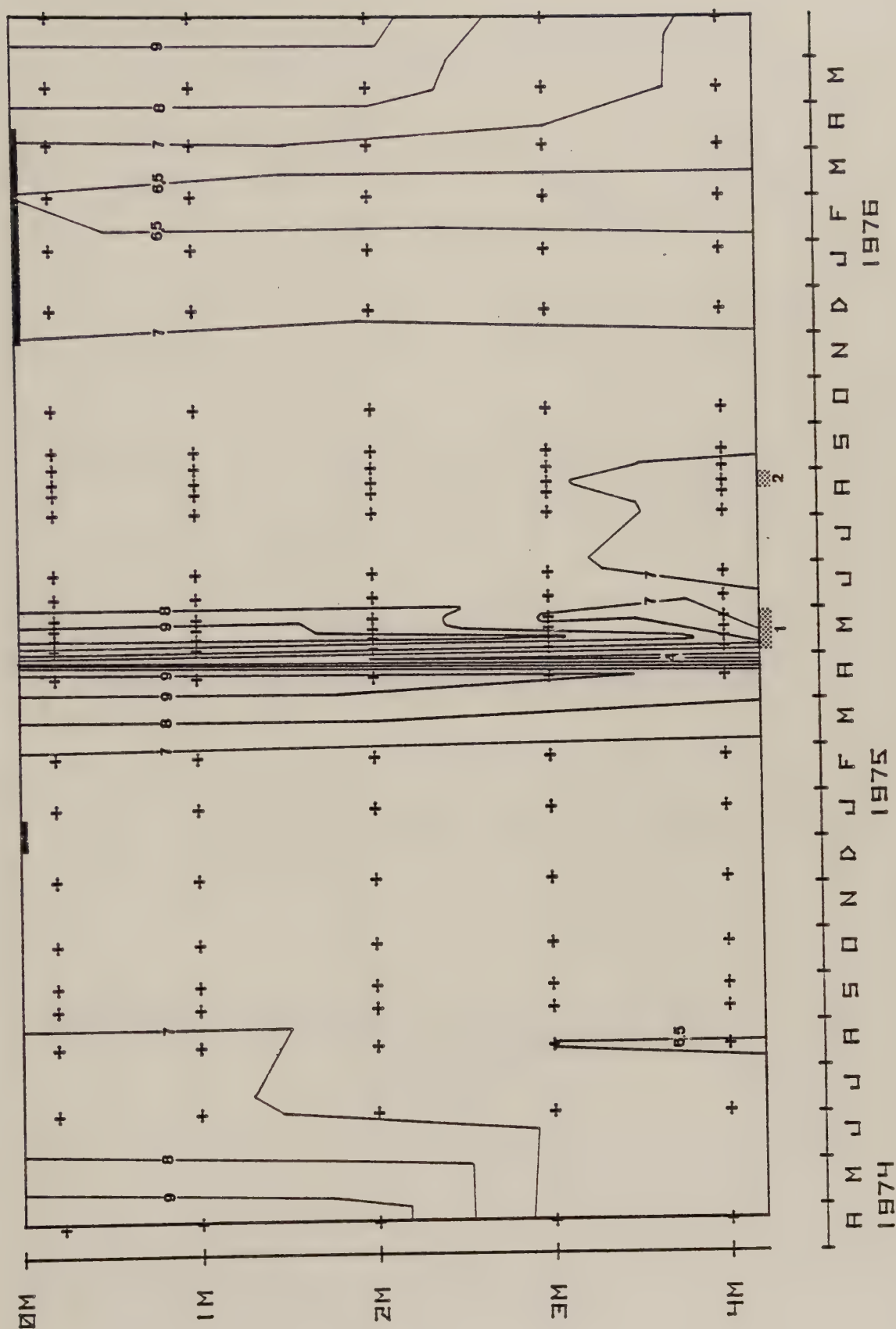


Fig 37) Time-depth diagram for pH in Lake Lillesjön.

LAKE LILLESJÖEN ALKALINITY ME/L

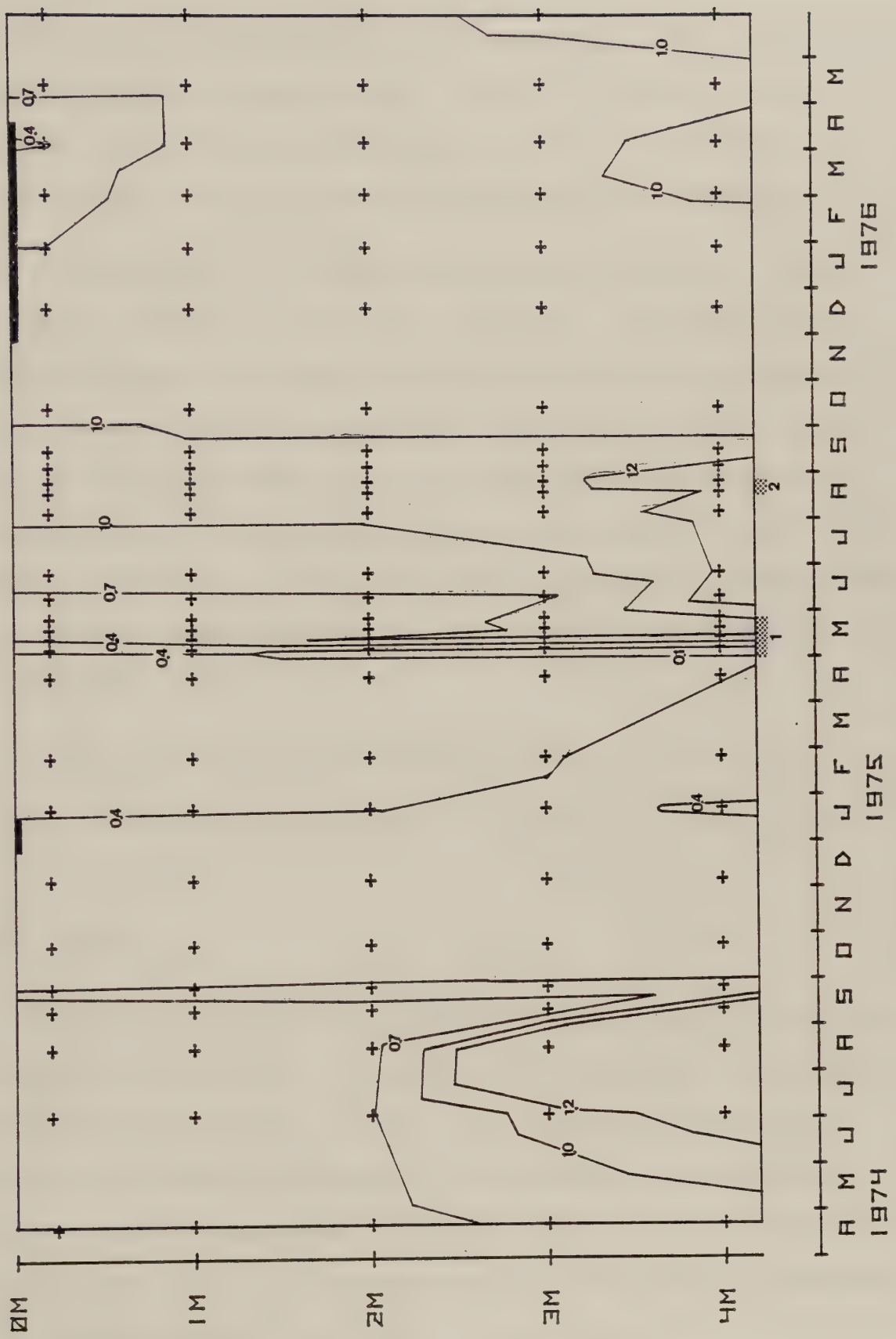


Fig 38) Time-depth diagram for alkalinity in Lake Lillesjön

This was traced to fermentation processes in the sediment (probably methane fermentation). Either no other suitable electron acceptors were available or none were utilized (SO_4 was analysed but no decrease was seen on this occasion).

After restoration the largest increase in inorganic carbon occurred in February 1976 under ice cover. However, on this occasion oxygen was present in all strata, and the increase in carbon was mainly registered in the shallow zones of the lake. Only 24 % of the total C increase was confined to the hypolimnion. High respiration of the submersed littoral vegetation contributed to this increase in inorganic carbon (after restoration Nitella sp. rapidly colonized the sediment down to a depth of about 2 m).

Alkalinity stabilized after restoration at about 0.7 meq/l or 30 % of the sum of anions, which is about the same as found before restoration.

6.2.4. Oxygen

One of the most central environmental factors to be directed in restoration efforts in damaged lake ecosystems is oxygen. As indicated in section 3.4.3., the presence or absence of oxygen in the water body and at the sediment-water interface controls development of bacterial communities, mobility of nutrients, etc. Thus the characteristics of the sediment are to a large extent decisive for metabolism of the entire lake.

Due to the high annual loading with macrophyte biomass, espe-

cially Lemna, and the funnel-shaped morphology of the hypolimnion, rapid deoxygenation occurred in the water body below 3 m water depth. The sediment had therefore permanently changed in structure and contributed, due to accumulated reduced substances, to the stabilization of anoxic conditions at the sediment-water interface.

The distribution of oxygen during the investigation period is shown in Fig 39. While anoxic conditions at the sediment-water interface during summer stagnation lasted for at least 5 months in 1974, the anoxic period during summer 1976 was greatly reduced by the sediment treatment and the reduced oxygen demand and nutrient recycling thus achieved. The period of completely anoxic conditions at the sediment surface was shortened to about 1.5 months. There was almost no ice cover during the mild winter 1974-1975. This led to an oxygenation of the sediment surface. However, the properties of the sediment were hardly changed, which was confirmed by oxygen demand studies (Sapromat) conducted on sediment in March 1975. The initial oxygen demand of the sediment was identical to that obtained in cores taken after summer stagnation 1974.

Before restoration, the distribution of oxygen in the epilimnion was a function of Lemna development. After a spring bloom of phytoplankton had resulted in supersaturation (160 %), oxygen saturation decreased to a minimum of 23 % at 0.5 m depth in September 1974. The oxygenation of the epilimnetic water was extremely slow. The water body became saturated with

LAKE LILLESJÖEN OXYGEN MG/L

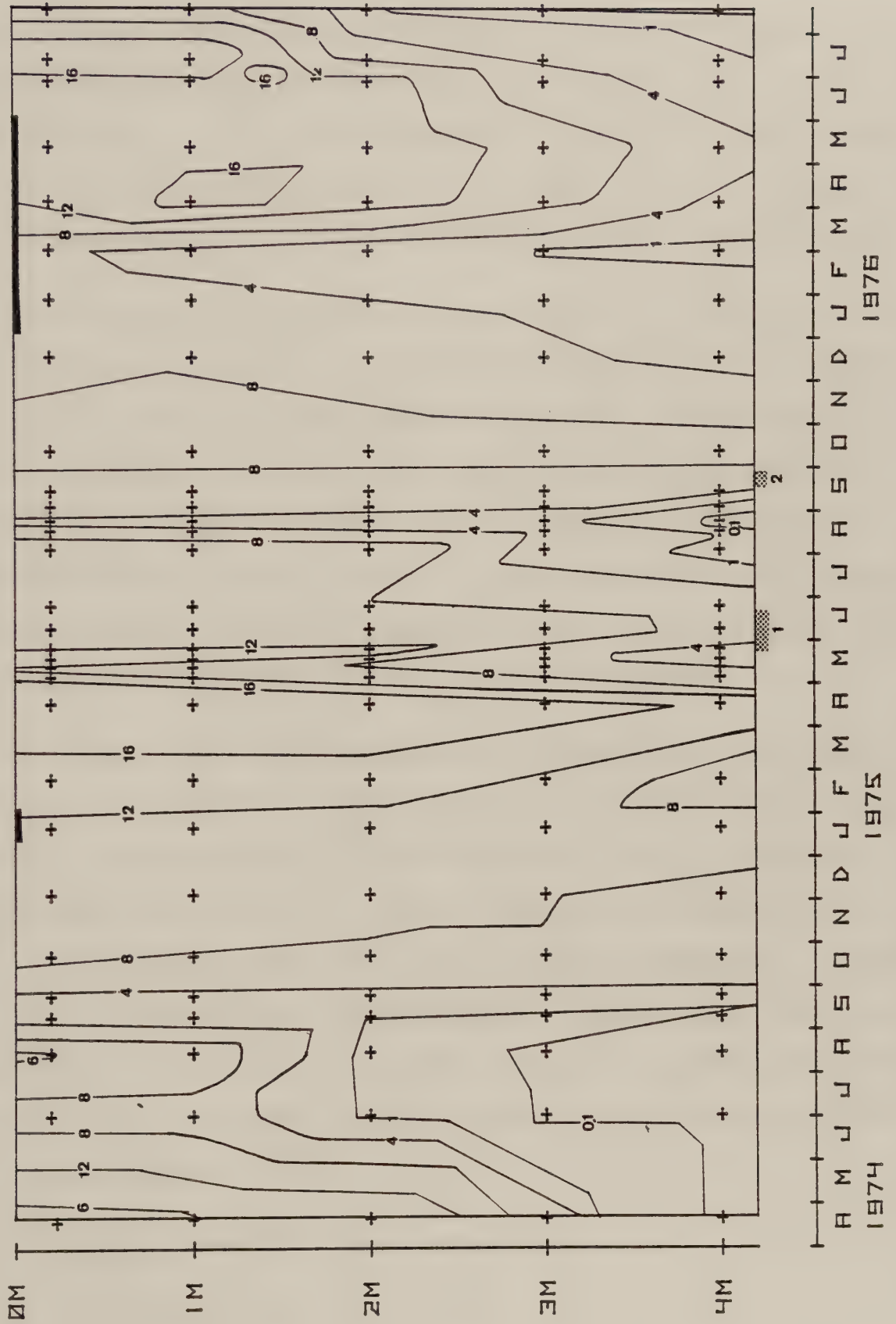


Fig 39) Time-depth diagram for oxygen in Lake Lillesjön.

oxygen during Februari 1975 only because of mild winter conditions and no permanent ice cover. A slightly inverted temperature profile (3.1°C at the surface and 3.7°C at the sediment-water interface) then resulted in a sharp decline of oxygen at 4 m depth (94 % O_2 saturation at 3 m and 42 % at 4 m depth).

After restoration the epilimnion was already close to 100 % O_2 saturation in October. Oxygen was present during the entire ice period, and the lowest oxygen saturation values were obtained in March 1976, with about 25 % saturation in the epilimnion and 4 % at 4 m depth. During spring and summer 1976, supersaturation with O_2 occurred in the epilimnion (140-150 %). Phytoplankton had replaced Lemna and had thereby changed the oxygen distribution and balance in Lake Lillesjön.

During winter 1976-1977, oxygen was seriously depleted ($0.1 \text{ mg } \text{O}_2/\text{l}$ at 4 m depth) by the end of Februari, and a fish kill occurred. Extremely poor light conditions due to a long and heavy snow cover prevented photosyntheses by Nitella. After this winter Nitella was replaced by Elodea canadensis. In summer 1977 oxygen concentrations were close to saturation indicating no excessive phytoplankton production. During winter 1977-1978, the lake was ice-covered for 5 months, and oxygen was present in the whole water volume.

6.2.5. Conductivity and ionic composition

Before restoration conductivity was highly variable. Values between 170 and $340 \mu\text{S}_{20}/\text{cm}$ were recorded, with a weighted

mean of 190. The higher values occurred in the hypolimnion where degradation processes contributed metabolites such as HCO_3^- (CO_2), NH_4^+ , S^{2-} , etc. Cations were solubilized in the sediment and transported to the hypolimnion and also accumulated through the lysis of sedimenting organisms. These processes were recorded especially during summer stagnation 1974.

Application of the chemicals at the sediment surface gave a strong response in conductivity distribution with depth. The relaxation phase after the additions is clearly indicated in Fig 40. In 1977 conductivity varied between 170 and 270 with a weighted mean of $180 \mu\text{S}_{20}/\text{cm}$.

Before restoration chloride was usually the dominating anion in Lake Lillesjön, contributing 50-55 % of the anionic composition (Fig 41). Alkalinity followed with 30-35 %. However, in the lower hypolimnion alkalinity sometimes comprised more than 50 % and was then followed by chloride.

Sulphate contributed about 10-15 %. While chloride is biologically inactive, alkalinity and under low redox conditions sulphate are subject to biological metabolism. The relatively low sulphate concentrations prevented a more accentuated sulphate reduction. Sulphate varied between 12 and almost 20 mg SO_4/l . H_2S occurred frequently in the hypolimnion, but only in minor concentrations (less than 0.3 mg S/l). However, before restoration SO_4 was depleted on some occasions in the interstitial water at 4 m water depth.

LAKE LILLESJÖEN CONDUCTIVITY M520

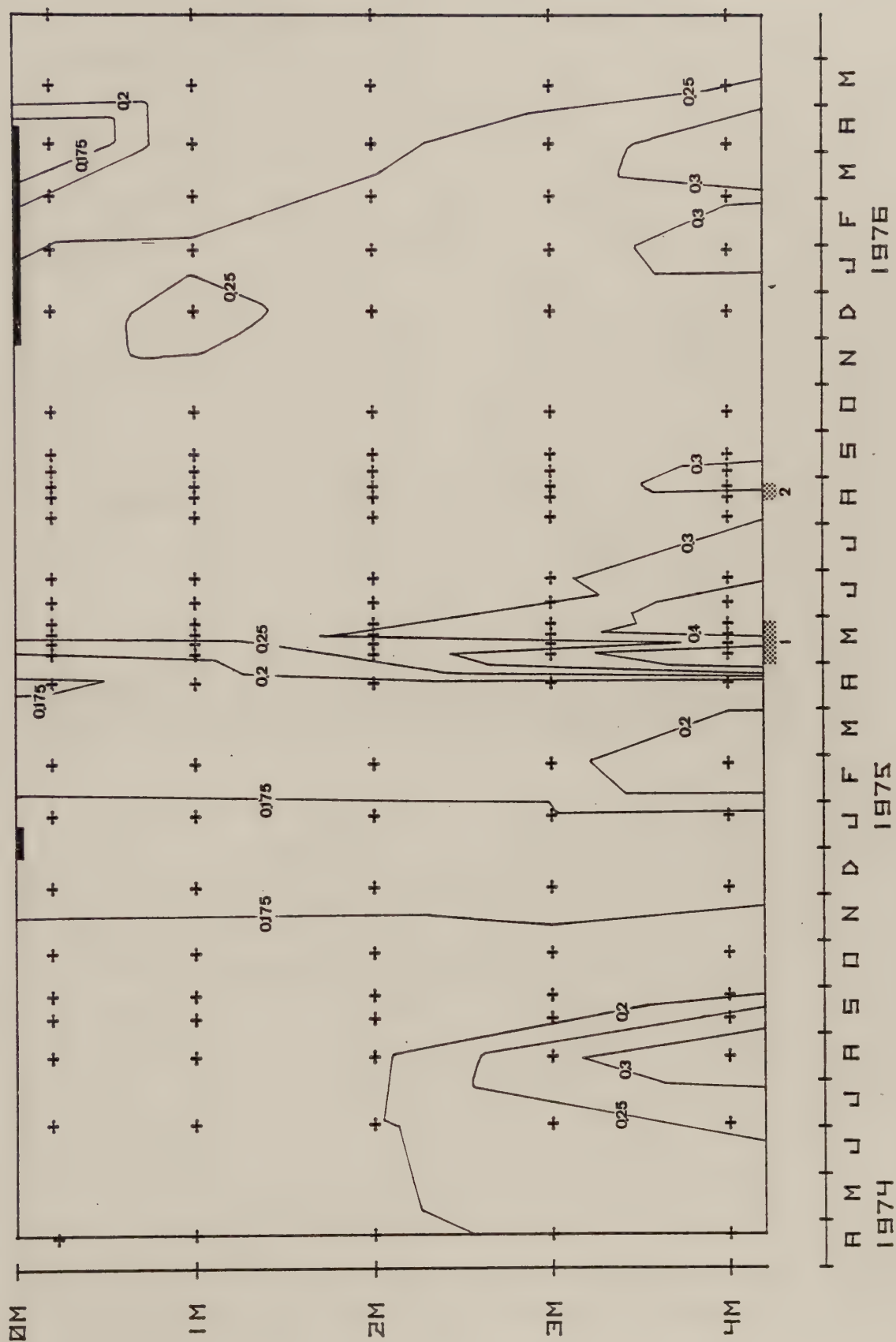


Fig 40) Time-depth diagram for conductivity in Lake Lillesjön.

LAKE LILLESJÖEN CHLORIDE MG/L

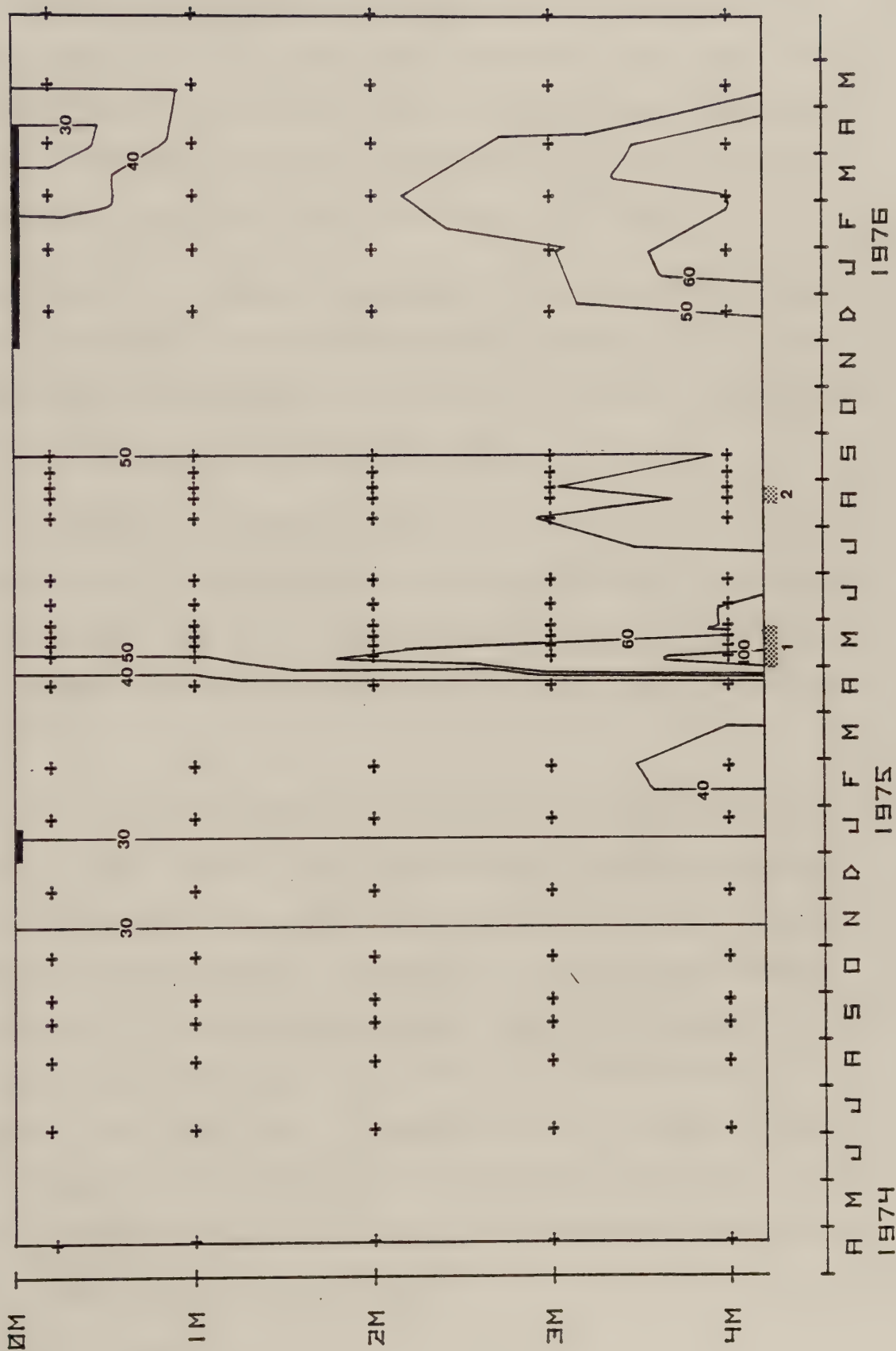


Fig 41) Time-depth diagram for chloride in Lake Lillesjön.

Before restoration the cation composition was dominated by calcium with 35-42 % of the cation equivalent sum. The additions of slaked lime and calcium nitrate during restoration enhanced this dominance, but concentration of calcium rapidly decreased again after sediment treatment (Fig 42).

Concentrations of sodium, magnesium and potassium remained unchanged during the entire investigation period. Both sodium and magnesium contributed 25-30 % while potassium contributed 4.5-5.5 % to the cation equivalent sum.

Large variations in ionic composition were caused by the large variation in NH_4 , especially in the hypolimnion. The maximum contribution by NH_4 to the sum of cations was recorded at the end of summer stagnation 1974. At 4 m depth, NH_4 then contributed 24 %.

By 1977 ionic composition had stabilized at about the same values as those found before restoration. Precipitation and dissolution of calcium carbonate in the sediment is mainly controlled by the partial pressure of carbon dioxide which is dependent on photosynthesis and respiration. Except on occasions when high pH was obtained due to high primary production, the water was not saturated with respect to calcium carbonate (1-20 % saturation). The high affinity of the sediment organic matter for calcium was probably responsible for the lowered calcium solubility.

At the end of 1977, the cation composition (% eq) was Ca 40 %, Mg 27 %, Na 28 % and K 5 %, and for the anions alkali-

LAKE LILLESJÖEN CA MG/L

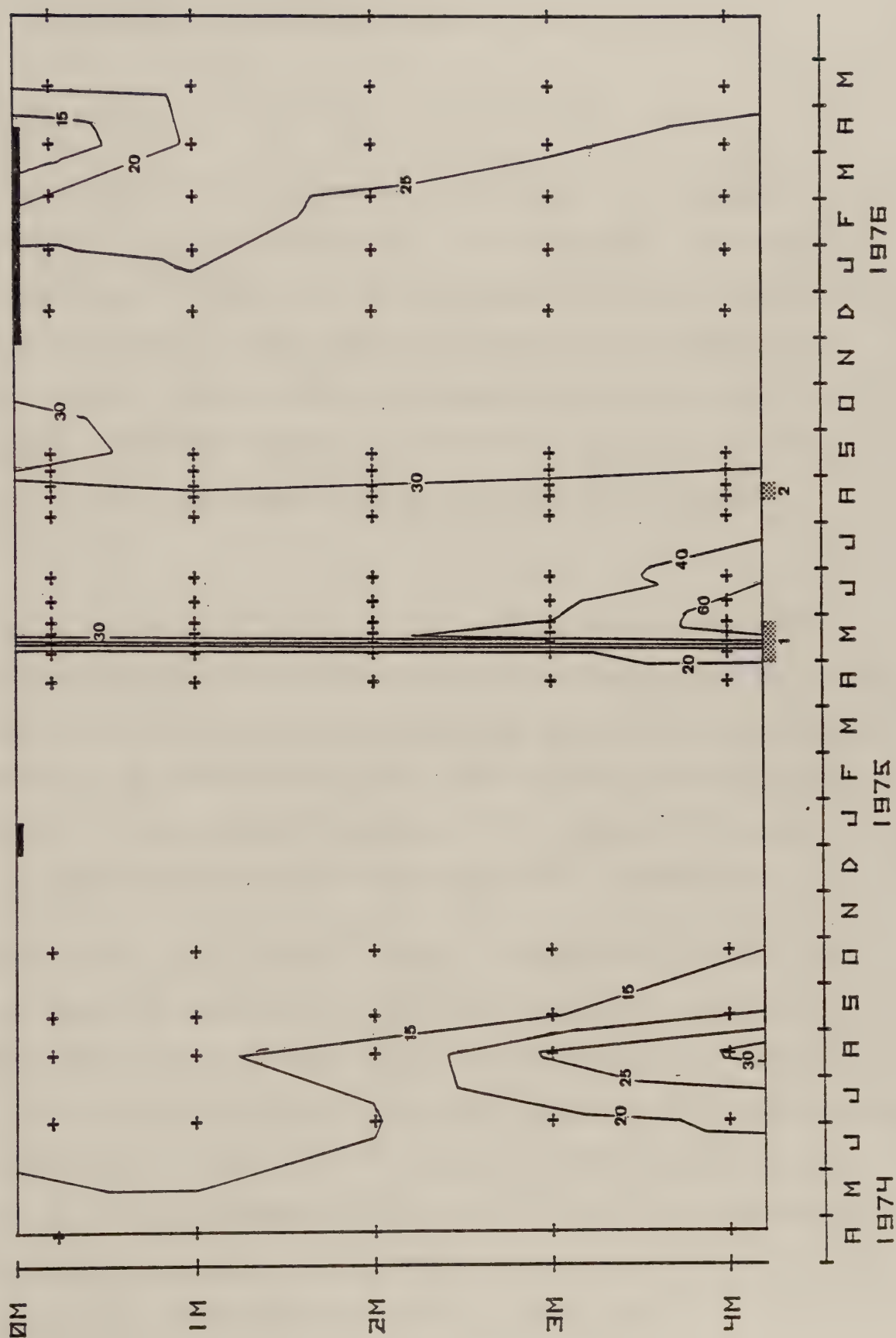


Fig 42) Time-depth diagram for calcium in Lake Lillesjön.

nity 30 %, Cl 50 % and SO_4 20 %.

6.2.6. Nutrients

Due to biochemical transformations the pools of phosphorus, nitrogen and carbon compounds are highly dynamic. Inorganic dissolved N and P fractions are instantly available for uptake by primary producers; the organic dissolved fractions are, however, easily transformed into compounds available for algal uptake. Turnover times for the individual nutrient fractions are thus controlled by organism abundance, activity and structure.

Input of nutrients to Lake Lillesjön after sewage diversion can be considered low with respect to phosphorus (10-30 $\mu\text{g P/l}$, or about 8-10 kg P/a). Nitrogen loading by rainwater and surface drainage can be estimated to about 500 kg N/a. These figures are based on P and N analyses done on 5 occasions on water from the main drainage ditch and rain water composition.

Internal budget calculations before restoration revealed that release from the hypolimnetic sediment surface in response to deoxygenation was rapid and intensive. During summer stagnation 1974 (April to the end of August) about 26 kg P was released from the sediment. The total P content in Lake Lillesjön was then 36 kg. During summer stagnation 1977 total phosphorus increased from 5.2 kg to 9.6 kg. The release was 4.4 kg P which is about 1/6 of the P release before restoration.

Improvements after restoration with respect to P release were also recorded under winter conditions. The winter 1974-1975 was extremely mild, and no stratification developed. However, in December almost 19 kg P was present in the water mass corresponding to a mean concentration of 0.22 mg P/l (Fig 43 and Fig 44).

After restoration maximum P contents at the end of winter stagnation in 1976, 1977 and 1978 were 6.5, 9.6 and 6.0 kg P, respectively. In winter 1978, during about 4.5 months ice cover, the phosphorus gain was 2.7 kg P.

Nitrogen budgets are difficult to obtain due to conversion processes with molecular nitrogen and other gaseous nitrogen compounds subject to exchange with air. Time-depth diagrams are given for $\text{NO}_3\text{-N}$ (Fig 45), $\text{NO}_2\text{-N}$ (Fig 46) and $\text{NH}_4\text{-N}$ (Fig 47). These parameters were chosen since they demonstrate nitrate distribution at, and the rapidity of nitrate decrease after, sediment treatment. The rapid denitrification process is also evident in the occurrence and distribution of nitrite.

Nitrite can be considered an intermediate in reduction of nitrate to molecular nitrogen.

$\text{NH}_4\text{-N}$, which increased about 53 kg in the Lake Lillesjön water mass simultaneously with nitrate addition, was contained as an impurity in the added calcium nitrate. However, increases of this order of magnitude were frequently observed before restoration during stagnation periods. A maximum concentration of 13 mg $\text{NH}_4\text{-N/l}$ was recorded in water at 4 m depth in August

LAKE LILLESJÖEN TOTAL-P MG/L

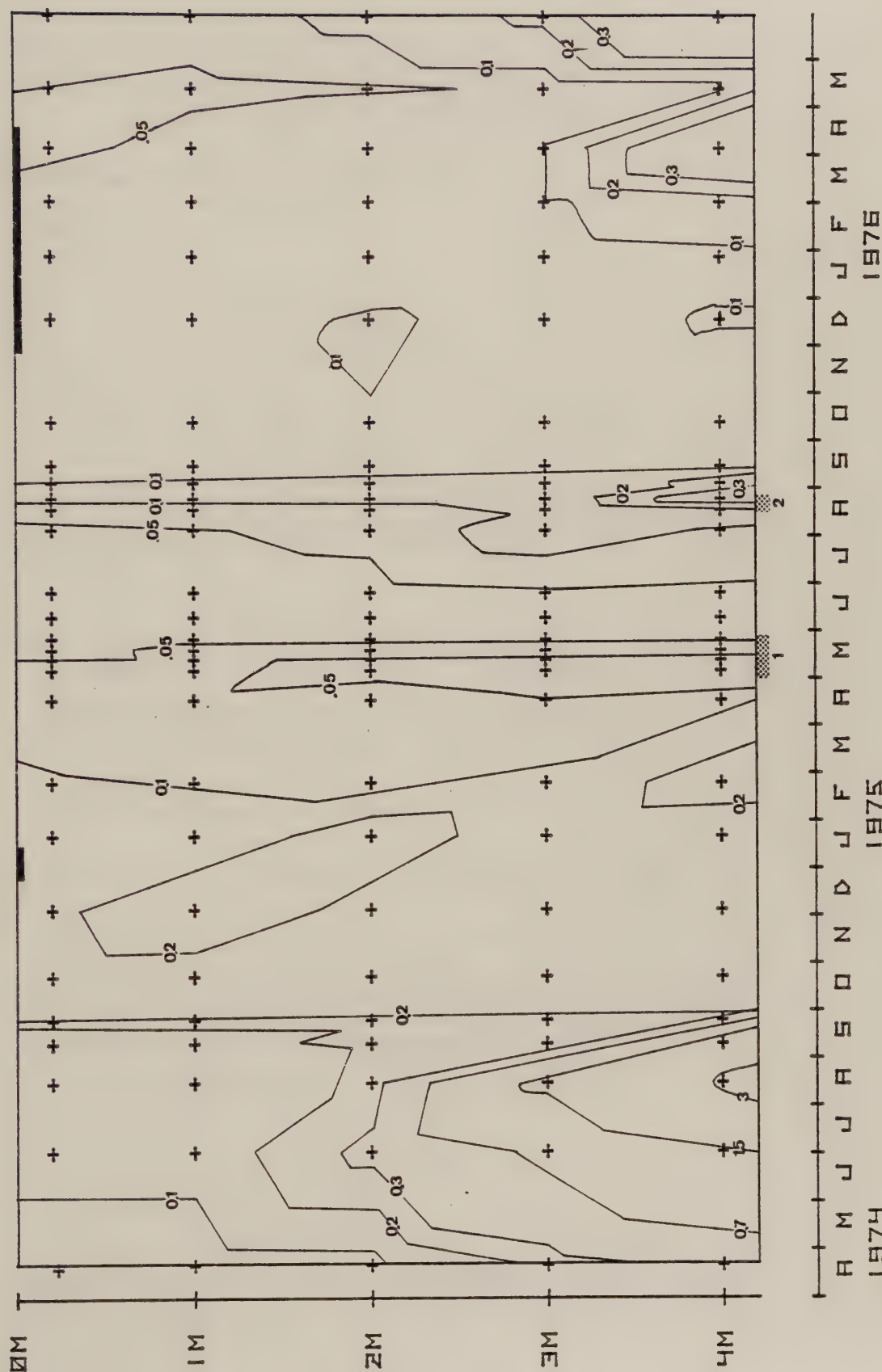


Fig 43) Time-depth diagram for total phosphorus in Lake Lillesjön.

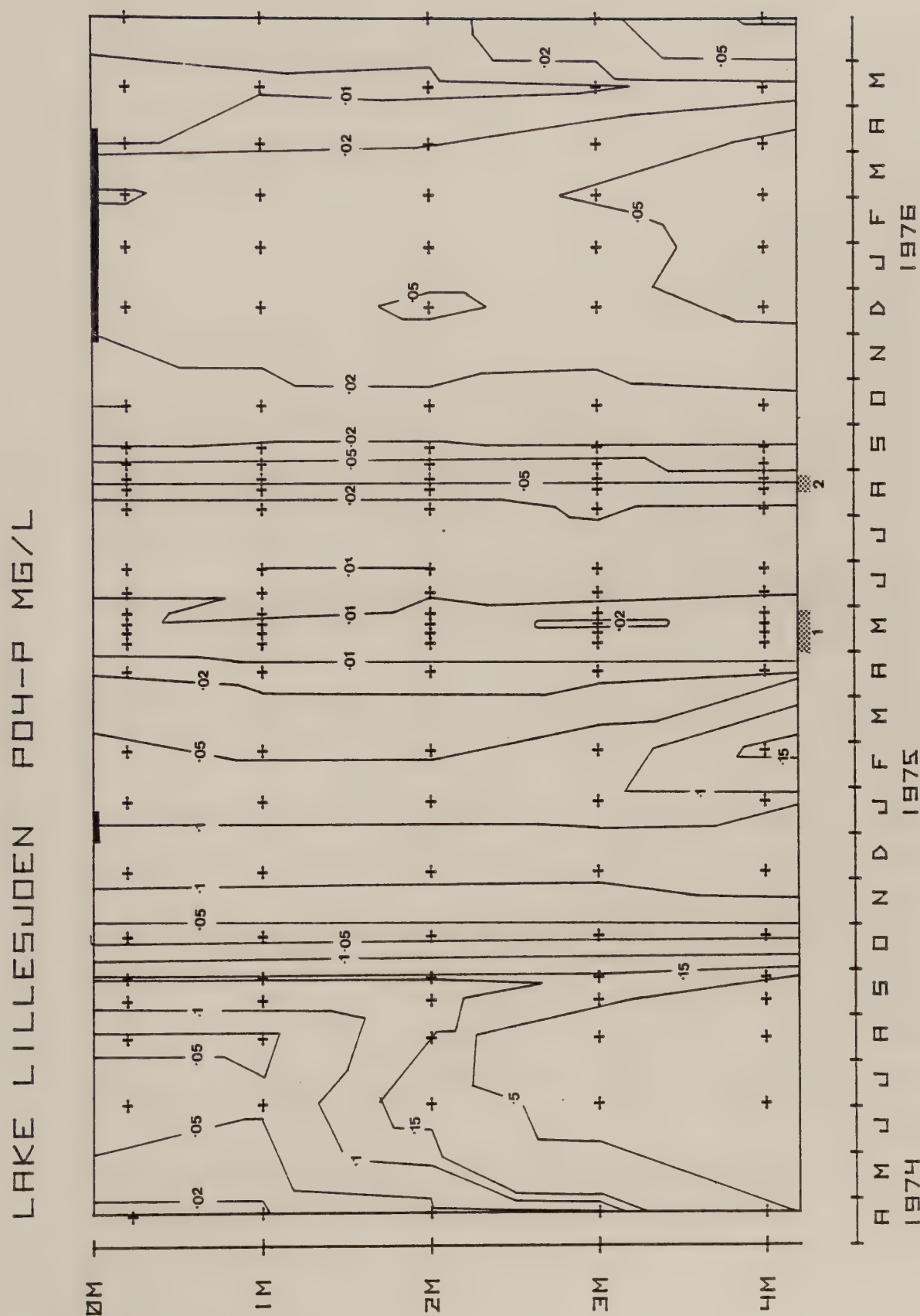


Fig 44) Time-depth diagram for phosphate phosphorus in Lake Lillesjön.

LAKE LILLESJÖEN NO₃-N MG/L

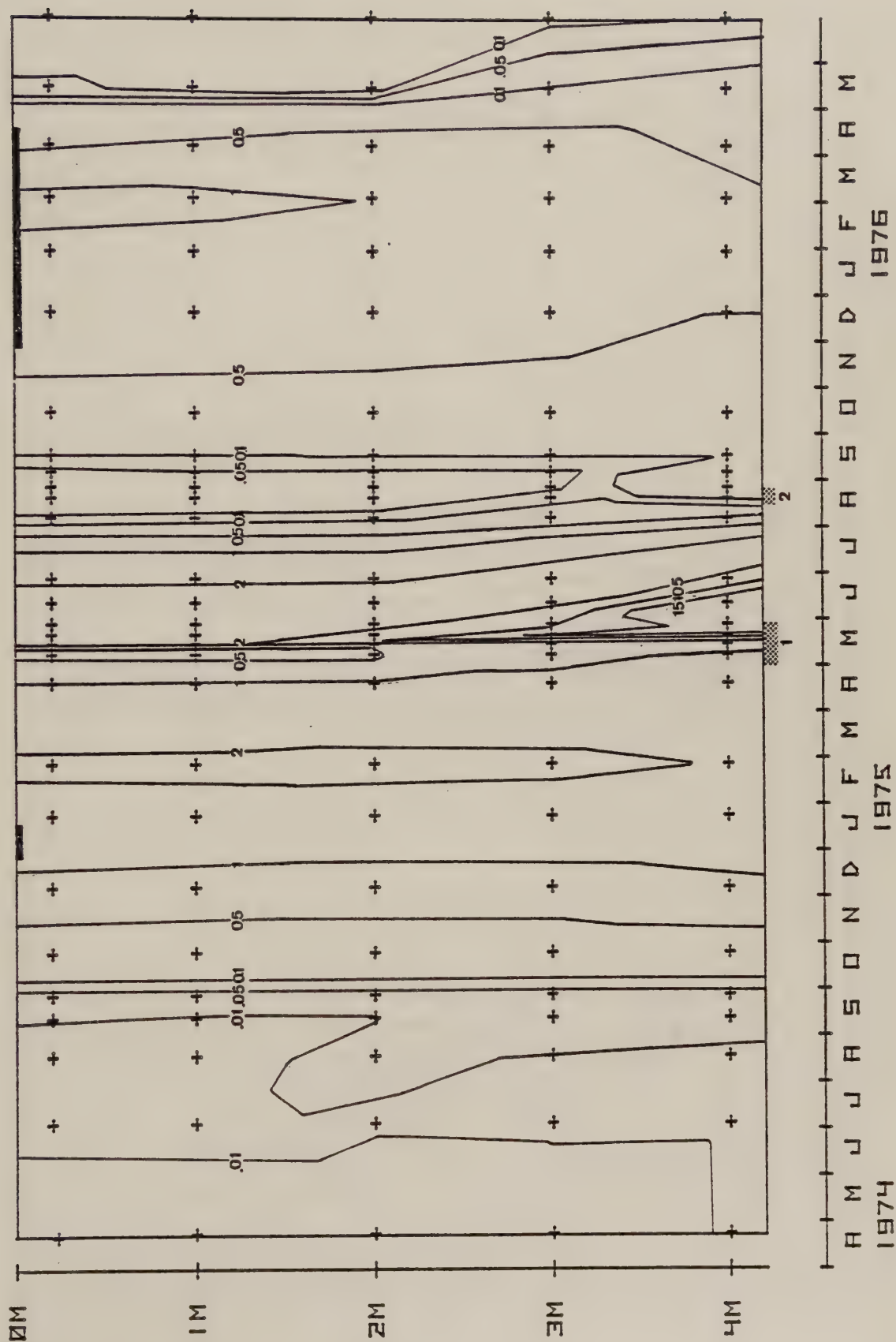


Fig 45) Time-depth diagram for nitrate nitrogen in Lake Lillesjön.

LAKE LILLESJÖEN NITRITE-N MG/L

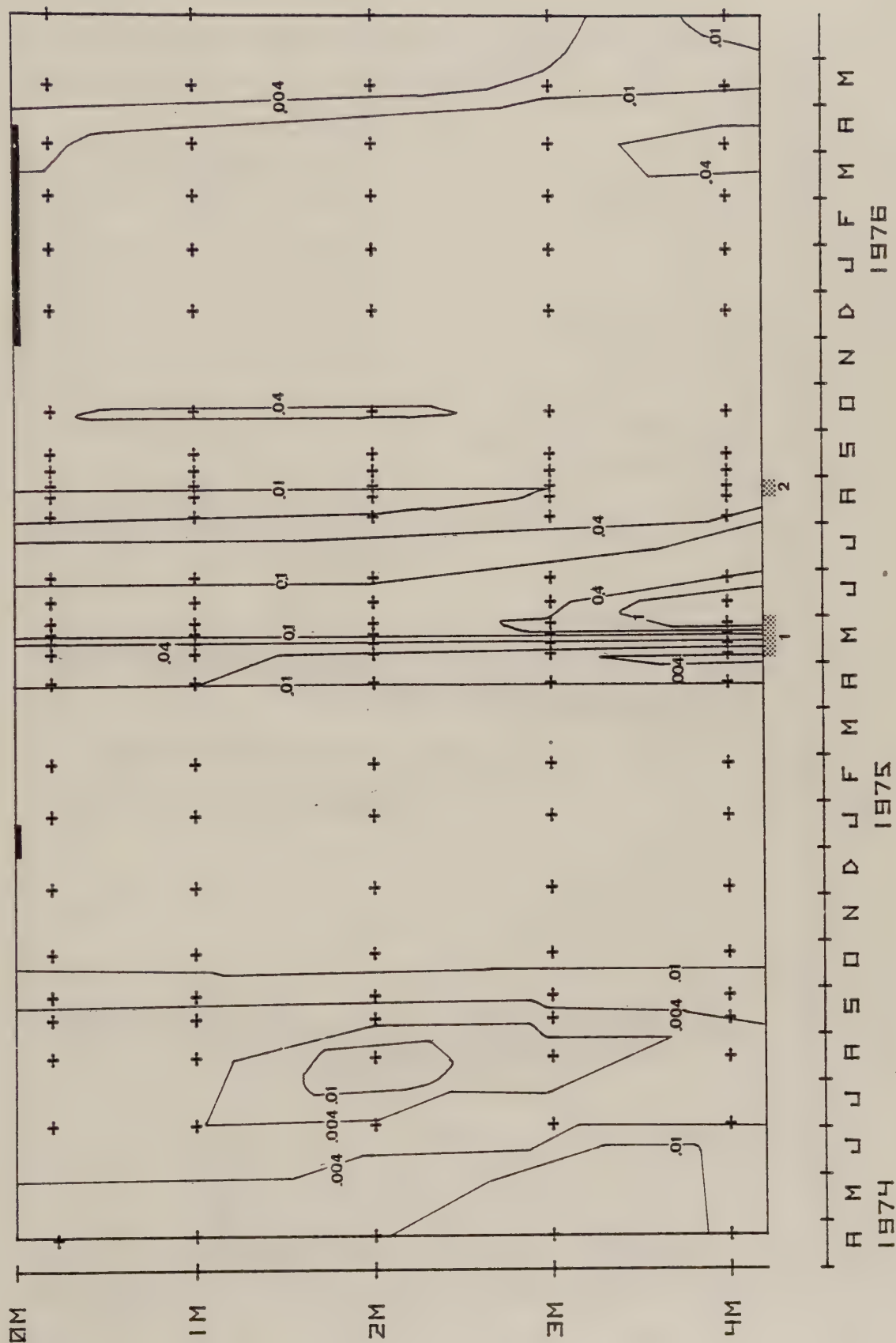


Fig 46) Time-depth diagram for nitrite nitrogen in Lake Lillesjön.

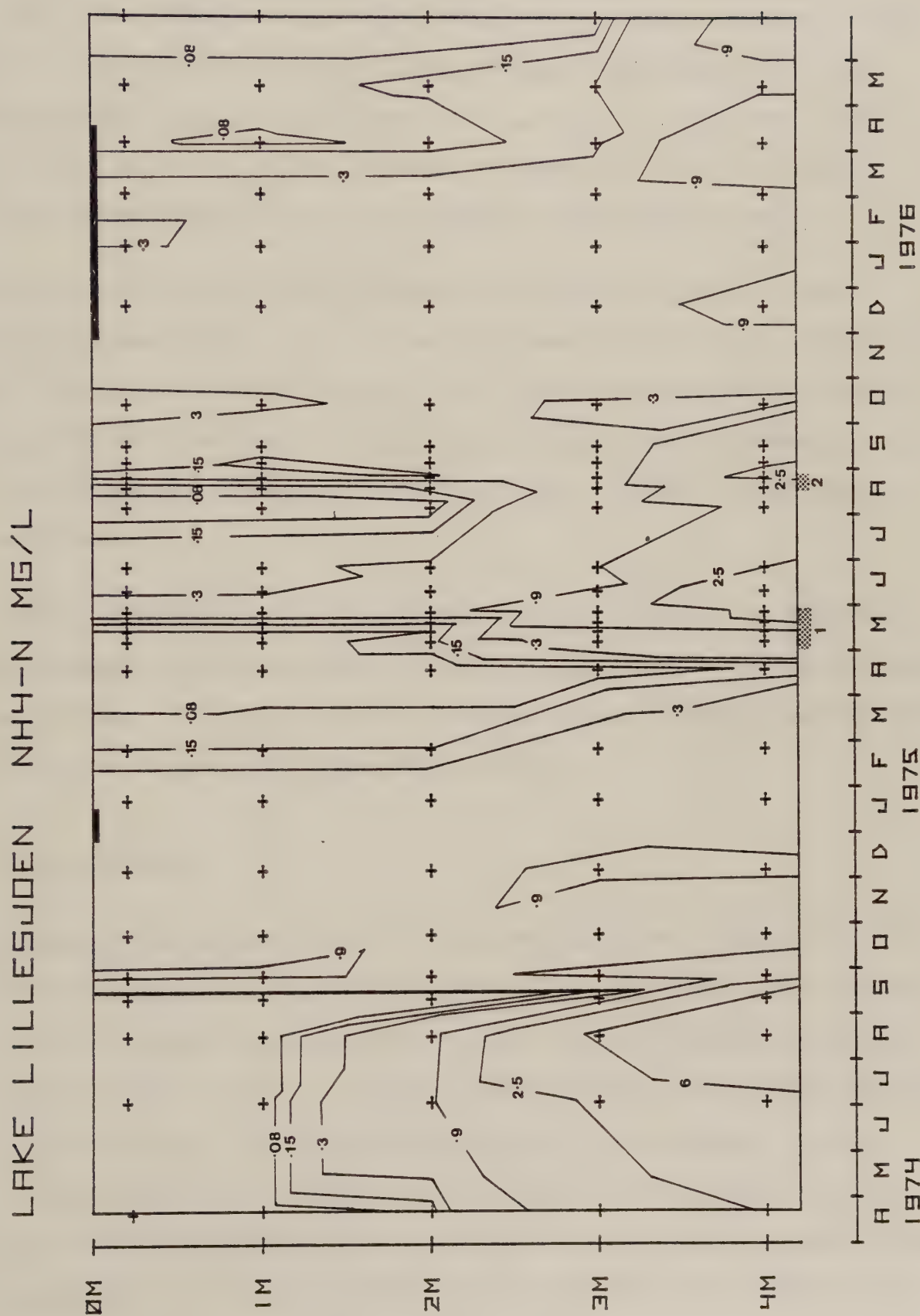


Fig 47) Time-depth diagram for ammonia nitrogen in Lake Lillesjön.

1974. The ammonia content of the lake had then increased with 90-100 kg to 120 kg $\text{NH}_4\text{-N}$ during summer stagnation. In 1977 the summer increase in ammonia N was only about 15 kg, giving a total of 30 kg $\text{NH}_4\text{-N}$. Release of ammonia from the sediment also decreased to 1/6 of the values before restoration.

Conditions during winter stagnation improved due to lower NH_4 release. While the increase in ammonia N during the period of ice cover 1975-1976 was 37 kg, the corresponding increase in 1977-1978 was only 25 kg. Nitrate increased, however, due to nitrification processes to 110 kg $\text{NO}_3\text{-N}$ at the end of winter stagnation.

Before restoration the dissolved organic N fraction amounted to between 0.3 and 1.0 mg N/l and the particulate organic fraction to between 0.1 and 0.6 mg/l. No significant changes due to restoration were seen in these parameters.

6.2.7. Silica

Although the depletion of silica coincided with abundance of diatoms during the investigation period 1974-1976, the characteristic bimodal pattern with minima during spring and autumn was not seen (Fig 48). However, during 1977 two minima occurred. In February 1977, 680 kg dissolved SiO_2 was present, corresponding to a mean concentration of 8.0 mg $\text{SiO}_2\text{/l}$. During spring the concentration decreased, and in June the total amount present was 90 kg SiO_2 . During summer stagnation the SiO_2 content in-

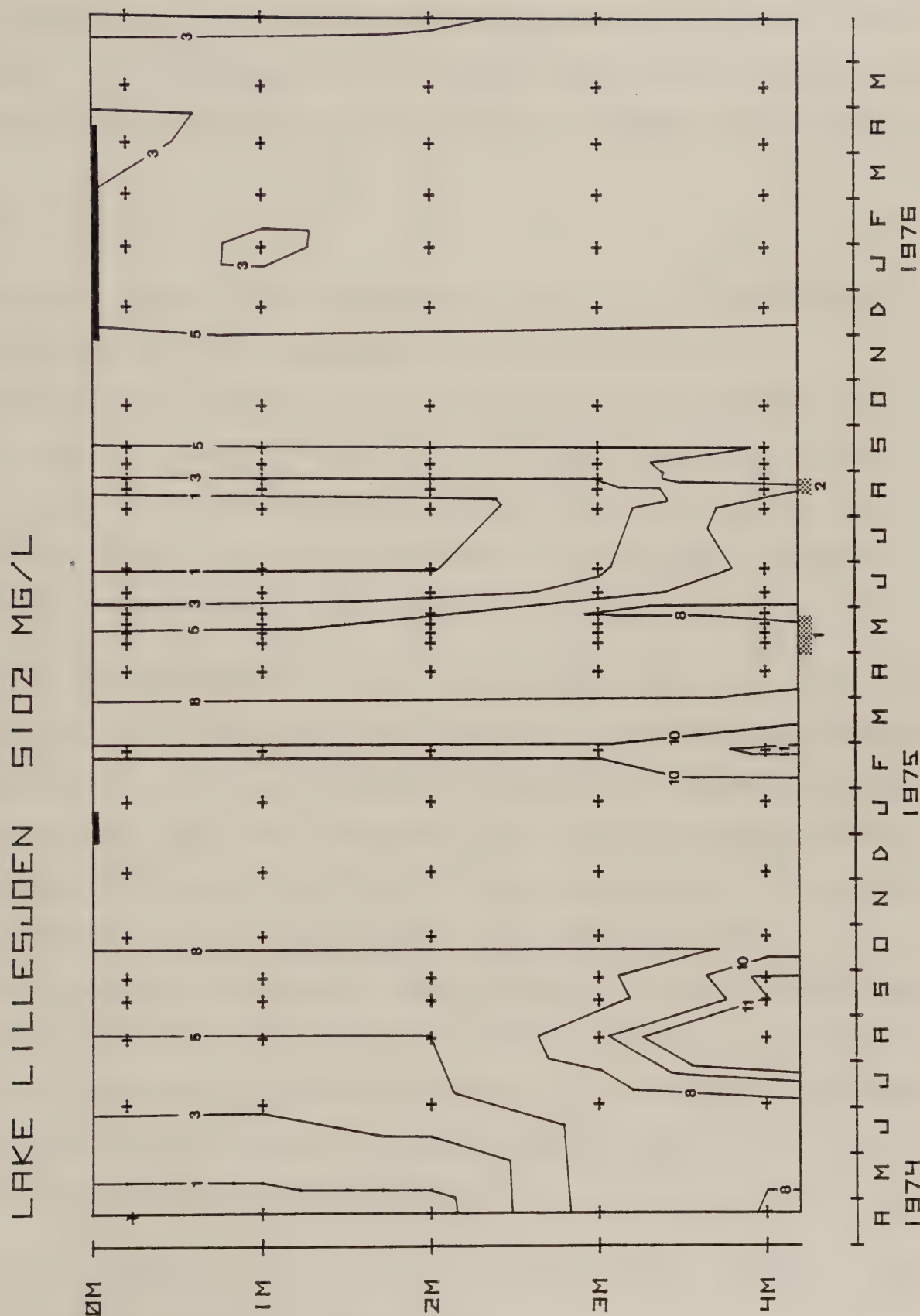


Fig 48) Time-depth diagram for reactive silica in Lake Lillesjön.

creased to 220 kg, while at the beginning of ice cover 40 kg SiO_2 , corresponding to 0.5 mg SiO_2/l , was present. During winter ice cover 1977-1978, 520 kg SiO_2 were released from the sediment.

6.2.8. Metals

Iron was added to the sediment as a part of the restoration treatment (cf. the time-depth diagram in Fig 49) to

- 1) enrich the sediment with a phosphorus-sorbing agent, and
- 2) enable a greater recycling of divalent iron which, when oxidized in oxygenated water, precipitates phosphorus.

Thereby water enriched in phosphate is restricted to layers in the deepest part of the lake.

While the enrichment of the upper sediment zone with iron failed due to rapid penetration and fixation of iron in lower sediment layers, the self-maintaining P precipitation mechanisms have functioned. When the macrophyte root felt was removed during August 1975, large amounts of P were released, but iron also accumulated in the water column. Weighted mean values of 1.2 mg Fe and 0.2 mg total P/l were recorded. During the following 20 days both iron and phosphorus were precipitated, and concentrations decreased to those found before the vegetation treatment. Maximum removal rates of $76 \text{ mg/m}^2 \cdot \text{d}$ and $19 \text{ mg/m}^2 \cdot \text{d}$ were calculated for iron and phosphorus, respectively.

After restoration the ratio by weight of dissolved Fe to total P in bottom water exceeds 5, while Fe:P weight ratios as low as 0.5 were obtained before restoration.

LAKE LILLESJÖEN FE MG/L

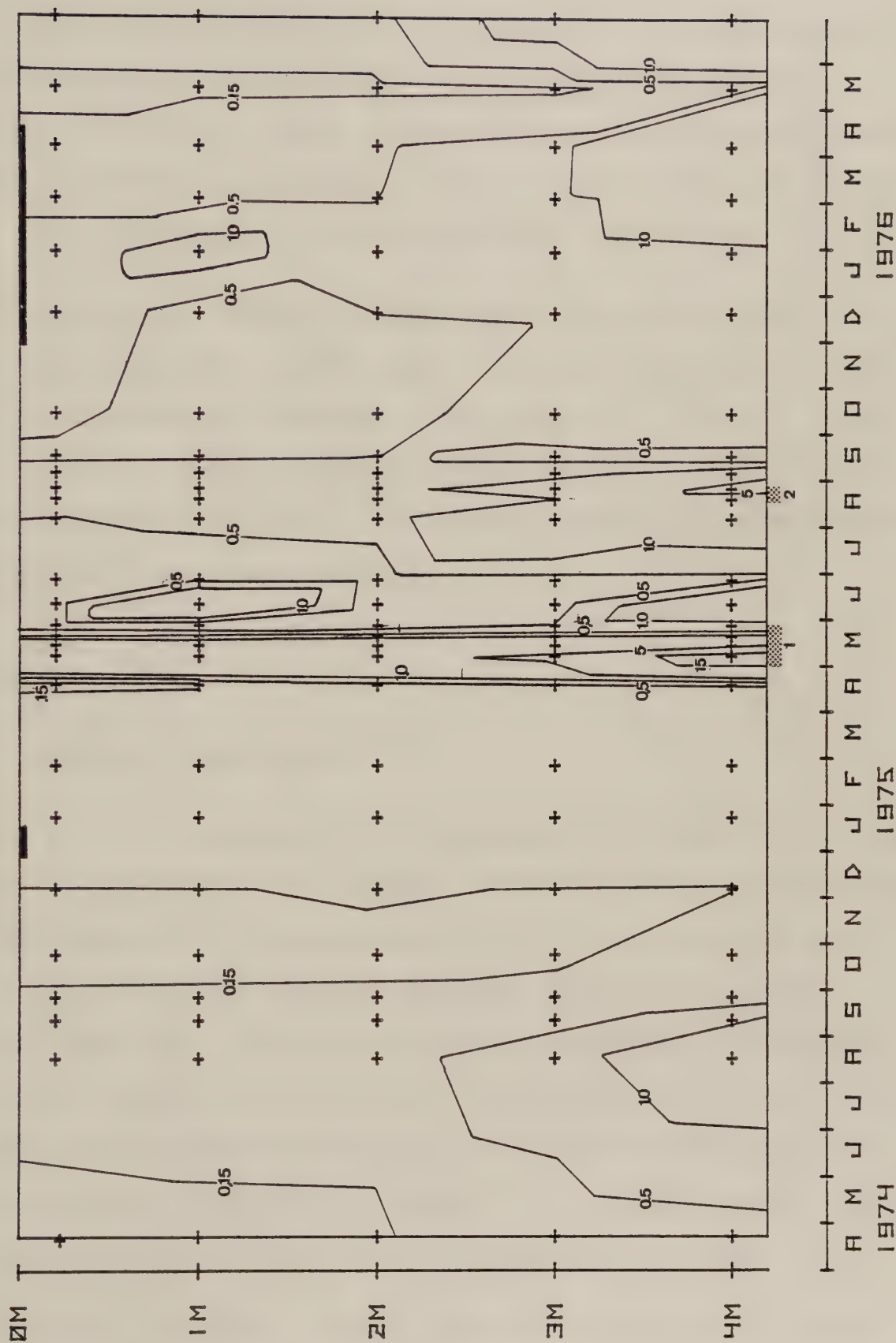


Fig 49) Time-depth diagram for iron in Lake Lillesjön.

Before restoration manganese concentrations in the epilimnion varied between 0.01 and 0.2 and in the hypolimnion between 0.03 and 0.9 mg Mn/l. After restoration manganese concentrations in the bottom water increased; at the end of stagnation periods, up to 2.3 mg Mn/l were recorded for water at 4 m depth.

Before restoration values of less than 0.01 mg Cu/l and 0.01 to 0.02 mg Zn/l were obtained. When iron was added to the sediment and pH decreased to a minimum, 0.08 mg Cu and 0.15 mg Zn were found. However, these concentrations decreased rapidly. On several occasions with anoxic conditions elevated Zn concentrations (0.06-0.09 mg Zn/l) were recorded.

6.3. Sediment

6.3.1. Sediment composition

Below 3 m water depth sediment composition on a dry matter basis changed little during the sediment treatment. At 4 m depth sediment was analyzed on 5 occasions (Fig 50). The restored sediment differs from the original sediment above all in resedimenting properties and the absence of sulphides. The sediment contained considerable amounts of sulphide before restoration, but this was removed by acidification with the iron solution. Thereby sediment properties changed from extremely slowly sedimenting, colloidal to readily sedimenting and granular.

The dry matter content, however, changed only slightly. Loss on ignition decreased about 3 % in the upper 25 cm layer, which proved to be significant. A significant decrease in Kjeldahl

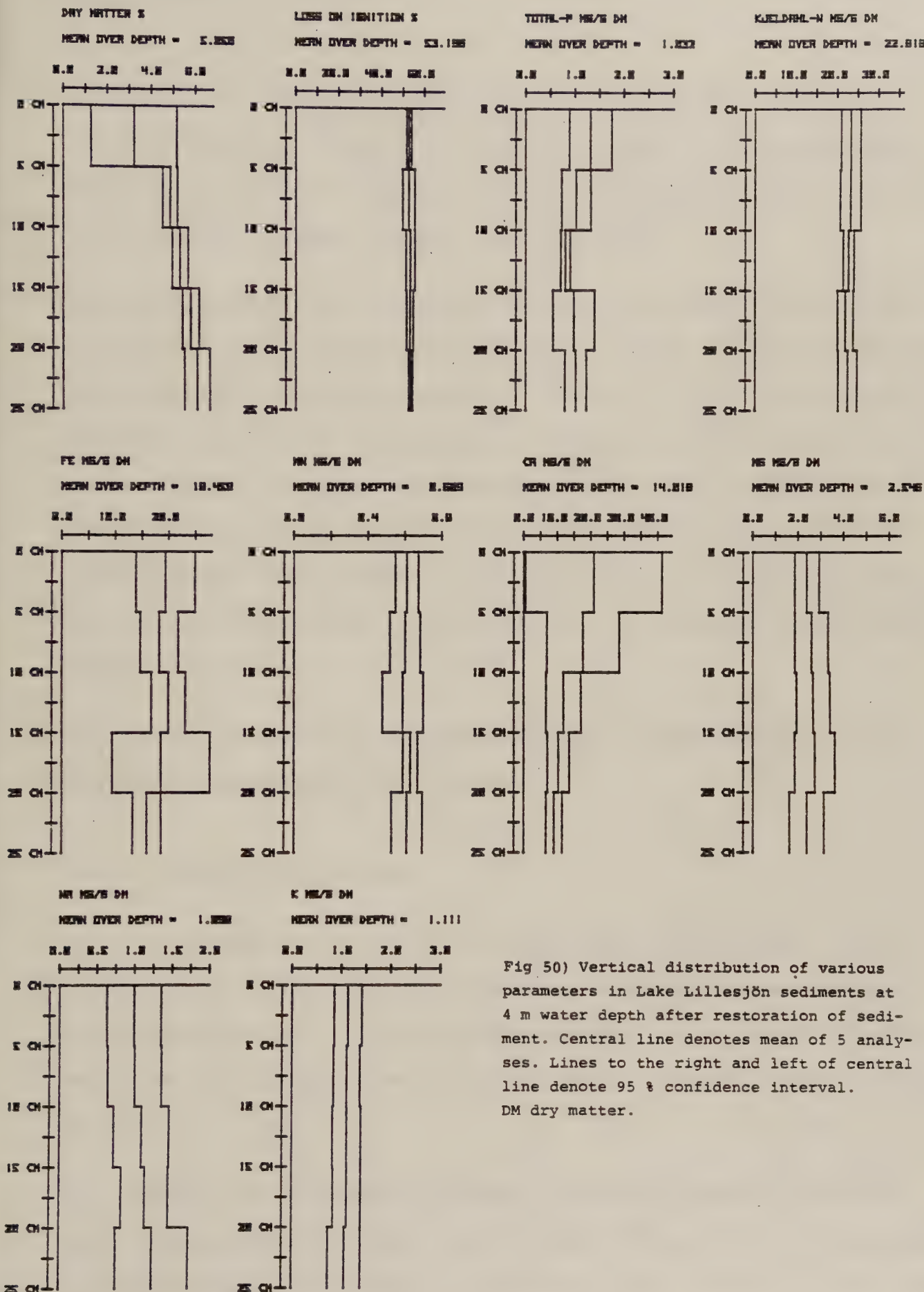


Fig 50) Vertical distribution of various parameters in Lake Lillesjön sediments at 4 m water depth after restoration of sediment. Central line denotes mean of 5 analyses. Lines to the right and left of central line denote 95 % confidence interval. DM dry matter.

nitrogen (7 %) was also observed in the upper 25 cm. The desired increase in iron on a dry matter basis was not achieved. Instead of concentration of iron in the upper 10-20 cm, considerably thicker sediment layers were affected.

Calcium, however, was strongly complexed by the organic matter and was fixed almost exclusively in the upper 15 cm. The greatly broadened confidence interval (Fig 50) in the upper 10 cm indicates a certain heterogeneity caused by restoration. The high affinity of humic substances for Ca ions greatly affected the mobility of the calcium solutions. Irreversible ionic exchange of Ca ions against Mg, Na, K and H is also likely since Mg, Na and K decreased in the upper 10 cm sediment layer after restoration.

All these changes were expected and were shown earlier in laboratory experiments (cf. Fig 21).

6.3.2. Interstitial water

The key to changes in the lake metabolism was believed to be interstitial water ion concentrations and their relations to hypolimnetic water. Therefore, the results of a successful sediment treatment should be reflected in interstitial water composition.

The results of interstitial water analyses obtained from sediment sampled at 4 m water depth during the period July-September 1975 were pooled, and mean values are given in Fig 51. As a result of sediment treatment, alkalinity and conductivity in the

LAKE LILLESJÖEN

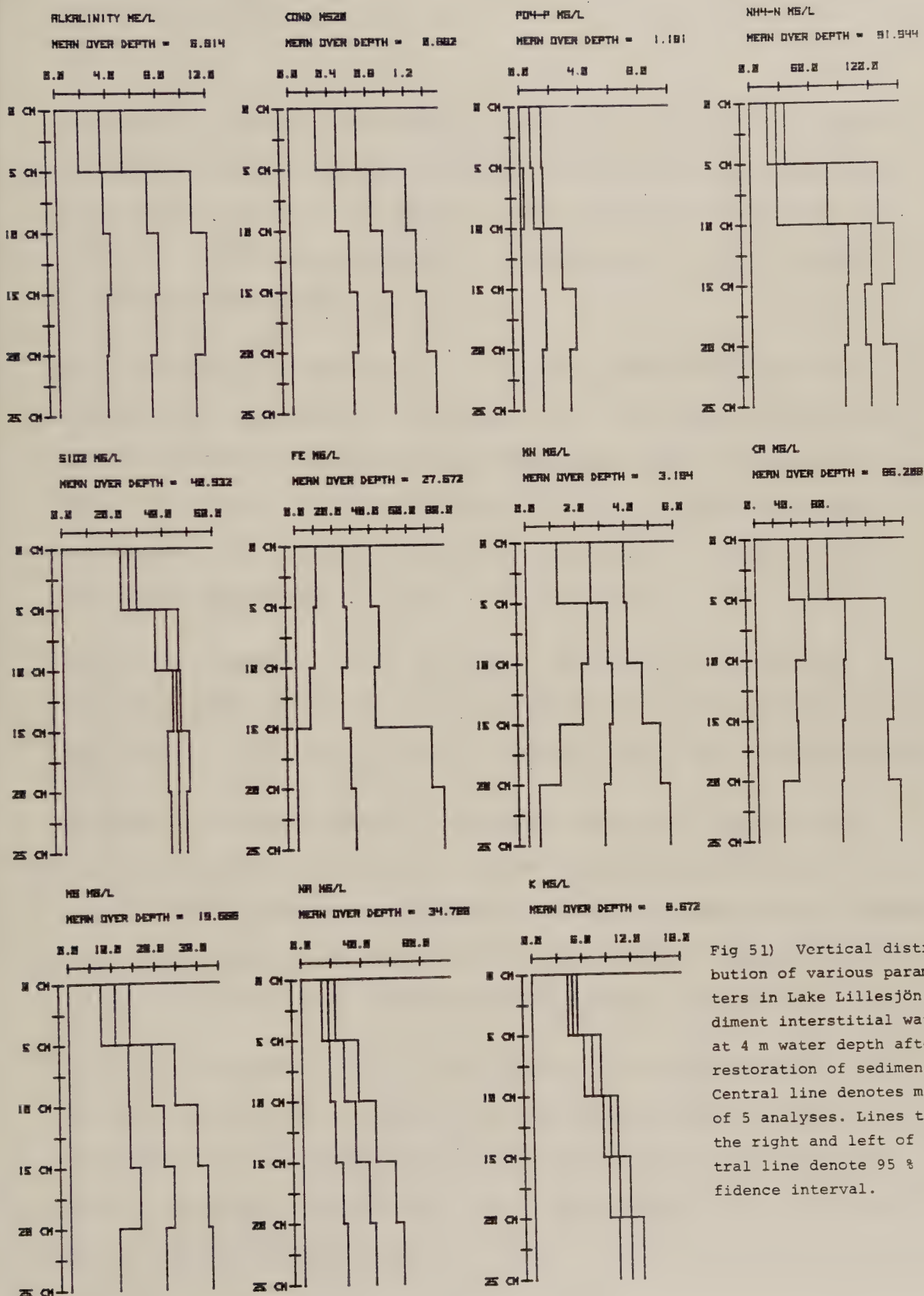


Fig 51) Vertical distribution of various parameters in Lake Lillesjön sediment interstitial water at 4 m water depth after restoration of sediment. Central line denotes mean of 5 analyses. Lines to the right and left of central line denote 95 % confidence interval.

interstitial water increased in the upper 25 cm layer. Despite the high denitrification activity, which should increase alkalinity by replacing the anion nitrate by bicarbonate, the increase in alkalinity was not so pronounced (c. 25 %). Conductivity increased with 76 %.

Due to an NH_4 content of c. 1 % in the added calcium nitrate, ammonia also increased with about 48 %. Other parameters which increased in interstitial water were iron, which increased 7 times to a mean concentration of 27.7 mg/l; manganese, which increased from 1.23 to 3.16 mg/l; calcium, 3.3 times, to 86 mg/l; and magnesium, 2 times, to 19.7 mg/l.

Silica decreased to 86 %, K to 66 % and Na to 48 % of the weighted mean values found before restoration. Phosphorus decreased from 7 to 1.2 mg/l, which is about 1/6 of the initial value.

Phosphate, ammonia and iron concentrations in interstitial water were also measured in 6 cores randomly sampled below 3 m water depth at the end of January 1976; and phosphate and ammonia were determined in another survey conducted in September 1977 on 10 cores randomly sampled below 3 m depth (Fig 52).

A slight increase in $\text{PO}_4\text{-P}$ was seen on the first occasion. A further increase was recorded on the second occasion at the end of summer stagnation when the worst conditions were expected. Ammonia gradually decreased, and on the second occasion interstitial water concentrations between 18 and 38 mg $\text{NH}_4\text{-N/l}$ were

LAKE LILLESJÖEN

3-4M 760127 N=6

PO₄-P MG/L

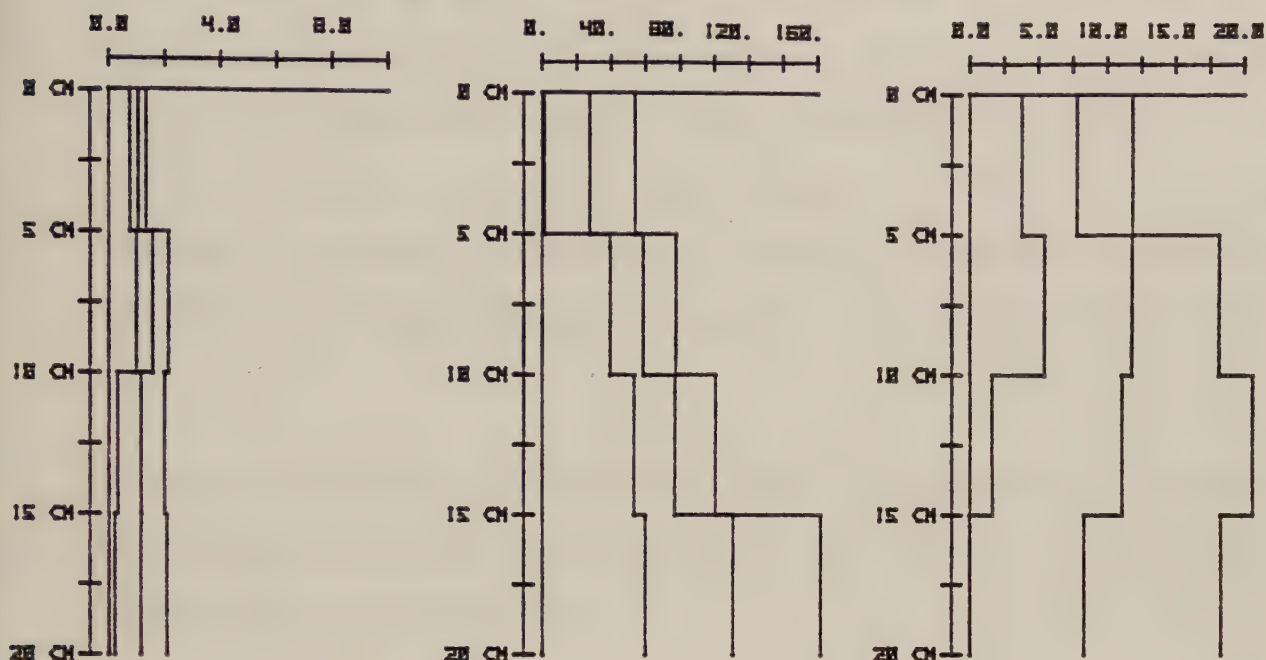
MEAN OVER DEPTH = 1.229

NH₄-N MG/L

MEAN OVER DEPTH = 68.533

FE MG/L

MEAN OVER DEPTH = 9.775



LAKE LILLESJÖEN

3-4M 770910 N=10

PO₄-P MG/L

MEAN OVER DEPTH = 1.953

NH₄-N MG/L

MEAN OVER DEPTH = 28.815

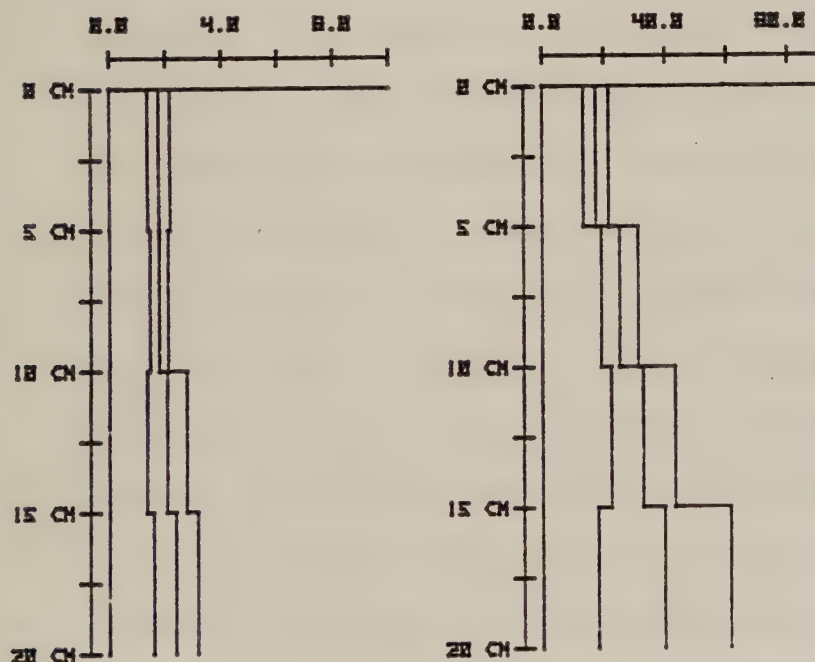


Fig 52) Surveys of nutrient (PO₄-P, NH₄-N and, on one occasion, Fe) concentrations in sediment interstitial water in Lake Lillesjön. For the first survey 76-01-27, the central line denotes mean of 6 analyses; for the second survey 77-09-10, the central line denotes mean of 10 analyses. Lines to right and left denote 95 % confidence interval. Samples taken at random over the treated area.

recorded. This is 40-50 % less than before restoration. The ammonia concentration in interstitial water at 4 m water depth was then of the same order of magnitude as that found in interstitial water at 3 m water depth before restoration. The decrease in ammonia is probably a result of nitrification-denitrification processes made possible by improved access to oxygen.

Iron showed decreased concentrations in interstitial water in January 1976 but had still more than twice the concentration found before restoration.

6.3.3. Sediment oxygen demand

Oxygen demand studies were conducted on several occasions after sediment treatment to follow the stabilization process after denitrification of the added nitrate. Due to the great abundance of denitrifying bacteria, stabilization is gradual, and not until the biomass of denitrifiers is reduced can a decrease in oxygen demand be expected. Oxygen demand after restoration was followed with 2 methods. Oxygen demand curves obtained by the Sapromat at 20 °C are directly comparable to the curves obtained on sediment before restoration (cf. Fig 14). The curves given in Fig 53 indicate the direction of changes in oxygen demand. The first set of curves, recorded in October 1975, were scattered over a considerable range. Then oxygen demand successively decreased and stabilized at 25-35 % of pre-restoration values.

LAKE LILLESJÖEN

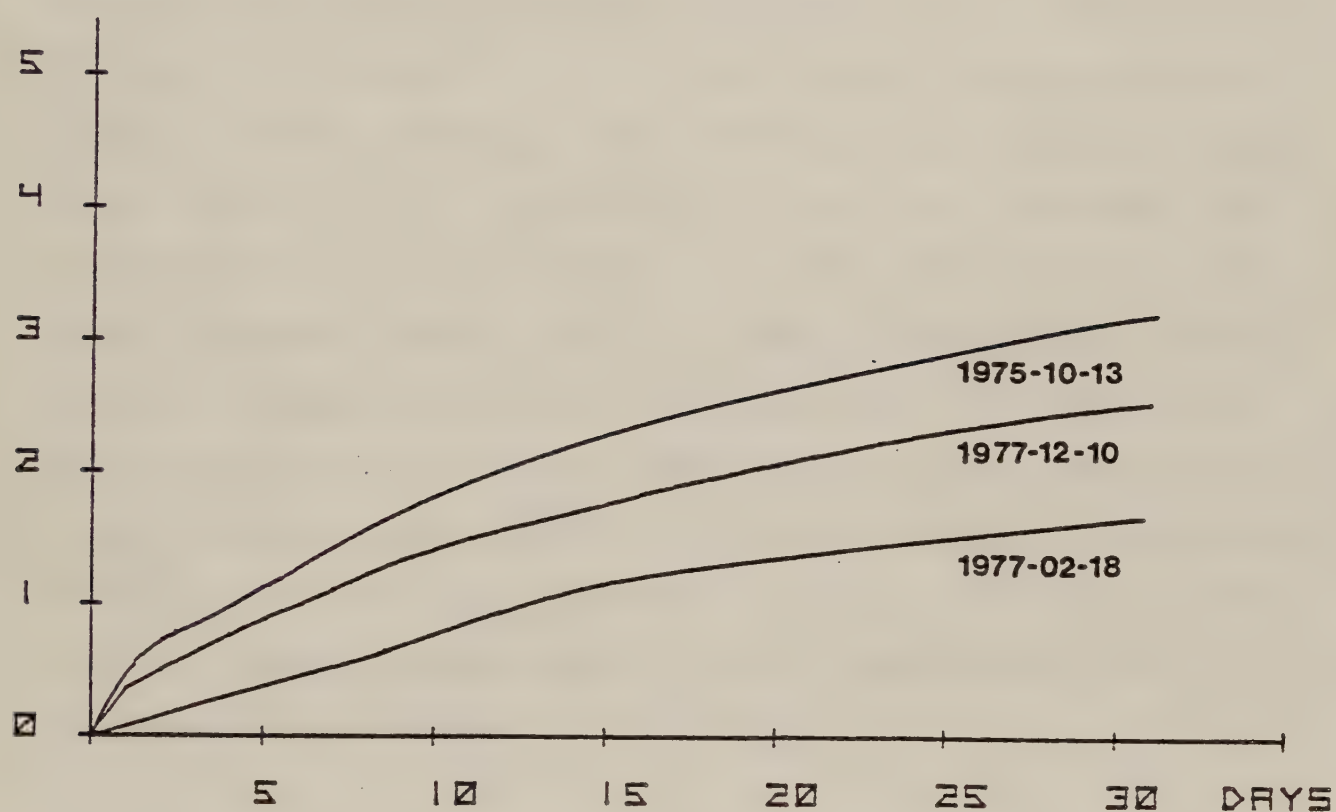
G O₂/L SEDIMENT

Fig 53) Oxygen demand (obtained with Sapromat at 20 °C) of Lake Lillesjön sediments sampled at 4 m water depth on various occasions after restoration.

In the other method (Granéli 1977 a), undisturbed sediment cores were taken at 4 m water depth, aerated to near saturation and incubated at in situ temperature. This method was used for 8 determinations, each with two cores, during the period October 1975 to February 1977. At the lowest incubation temperature (4.6 °C on 770221), values of 9.2 and 13.6 ml O₂/m².h were recorded. The highest values were obtained at 15 °C (760629) with 33.9 and 43.3 ml O₂/m².h. All values refer to rates obtained close to oxygen saturation. The weighted mean value for a year was c. 22 ml O₂/m².h. This value can still be considered high, corresponding to values found in sediments of eutrophic lakes (Lake Vombsjön, Granéli 1977 b). These values further indicate that the limited hypolimnion is highly sensitive, and anoxic conditions can easily result from sediment respiration, especially during summer stagnation at maximum sediment temperature. However, the diminished phosphorus recycling after restoration led to a highly reduced load of fresh organic matter and further decreased oxygen demand.

6.4. The organism community structure

6.4.1. Phytoplankton

Before restoration the presence of Lemna during summer stagnation limited development of phytoplankton. However, after ice break 1974 a mass development of diatoms occurred. On the first sampling occasion (770422) silica was depleted in the epilimnion (0.1 mg SiO₂/l), and pH was at a maximum (9.8) due to vigorous

primary production. Phytoplankton biomass (fresh weight c. 7 mg/l) was dominated by Synedra sp. Chlorophyta (Coelastrum microporum) dominated during August 1974 with a biomass of almost 12 mg/l, while Cryptomonas rostratiformis and Cryptomonas spp. dominated the phytoplankton in autumn 1974. The development of Lemna was at a maximum during August. Plankton samples were taken in the open water, occasionally free from Lemna. Low biomass values (0.3-0.5 mg/l) were recorded during winter, although good light conditions existed due to lack of ice cover. Cryptomonas spp. and Mallomonas akrokomos dominated during the period December 1974-January 1975. From the end of February until April, biomass again increased and Eudorina elegans dominated. Phytoplankton conditions during summer 1975 were strongly influenced by the restoration measures: sediment treatment and removal of macrophytes.

After restoration two characteristic changes in phytoplankton structure were observed: 1) The occurrence of large amounts of Volvox aureus in both autumn 1975 and summer 1976, and 2) an increase in nanoplankton.

The development of Volvox aureus, especially in the lower epilimnion where phosphorus increases and light is still available, is probably transitional. Further stabilization of the ecosystem and a higher diversity in the phytoplankton community can be expected. The increase in nanoplankton noted in spring 1976 is probably characteristic for lakes in a state of oligotrophication and was also recorded in Lake Trummen after restoration (Gelin & Riip 1978). Phytoplankton biomass, distribution

and transparency values are given in Fig 54.

During 1977, spring and autumn diatom maxima developed. Both were dominated by Asterionella formosa. During summer 1977 phytoplankton was dominated by Synura peterseni, but Volvox aureus was still abundant. However, due to the reduced sampling frequency during 1977, it is possible that other phytoplankton species became dominant but were not recorded.

6.4.2. Zooplankton

Zooplankton was only investigated semiquantitatively in net samples (cf. section 2.4.). Before restoration Lake Lillesjön was characterized by a dominance of heterotrophic processes. This was shown by appreciable supersaturation with CO₂ and low oxygen saturation (cf. section 6.2.3. and 6.2.4.). Zooplankton was dominated during summer 1974 by rotifers such as Brachionus urceolaris, Hexarthra mira, Keratella testudo and Polyarthra sp. Even cladocerans were present in considerable numbers. However, this group was exclusively represented by Daphnia pulex which was richly pigmented, especially when oxygen concentration was low. During winter 1974 and spring 1975 Brachionus angularis, Filinia longiseta and Keratella sp. dominated among rotifers. Daphnia pulex was succeeded by copepods, in May 1975 represented by Mesocyclops sp., Cyclops sp., Eudiaptomus gracilis, nauplii and copepodites.

In autumn 1975 after restoration rotifers again dominated the zooplankton. Keratella cochlearis was the dominant species un-

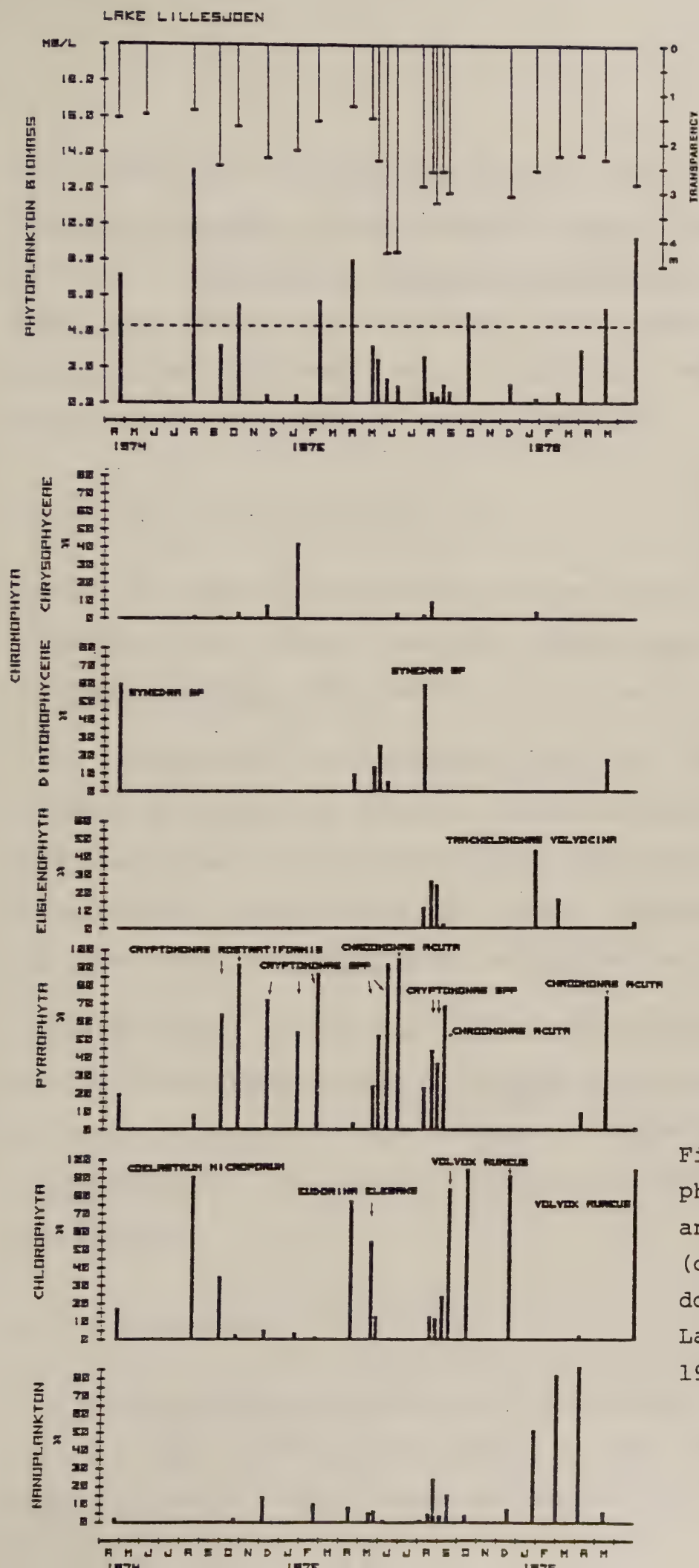


Fig 54. Transparency, phytoplankton biomass and community structure (distribution in % and dominant species) in Lake Lillesjön 1974-1976.

til January 1976 when Filinia longiseta dominated. In May 1976 Keratella quadrata became dominant. Daphnia pulex was not recorded, but Daphnia sp., Bosmina longirostris and Diaphanosoma brachyurum were observed instead. Among copepods Eudiaptomus gracilis was most common after restoration. Even nauplii and copepodites were abundant on all occasions.

6.4.3. Macrophyte vegetation

During the second restoration step most of the rooted macrophyte vegetation was removed, and only a small stand consisting mostly of Typha latifolia was spared (cf. section 5.5.).

After restoration the bottom area down to c. 2 m water depth was invaded by Nitella sp. However, during winter 1976-1977 a long and heavy snow cover prevented light penetration and Nitella disappeared. During summer 1977 Elodea canadensis colonized about the same area that Nitella had covered before.

Despite removal of roots of vast stands of nymphaeids during restoration, some Nymphaea alba and Nuphar luteum developed again, although in greatly reduced stands. No expansion of reeds or Calla palustris was recorded. Calla was greatly abundant before restoration.

6.4.4. Zoobenthos

Two surveys of the zoobenthos were conducted. One before (750421) and one after (760521) restoration. In both surveys sediment from 2, 3 and 4 m water depth was sampled (cf. section 2.6.).

Before restoration the following species and animal groups were found at 2 m water depth: Herpobdella octoculata, Asellus aquaticus, Chaoborus flavicans, Chironomini and Tanytarsini. Chironomidae dominated with 95 % of total numbers. Chironomini had an abundance of 650 per m^2 and Tanytarsini 200.

105 Chironomini and 1720 Chaoborus flavicans were found per m^2 at 3 m water depth. On this occasion oxygen was strongly supersaturated at this depth due to phytoplankton development. Oxygen was also present at 4 m depth on this occasion but the zoobenthos consisted exclusively of Chaoborus flavicans ($1600/m^2$). Chaoborus survived oxygen-free periods at 4 m in Lake Lillesjön due to its ability to migrate in a diel pattern to epilimnetic waters containing oxygen (Berg & Petersen 1956).

After restoration the number of Chironomini decreased to $52/m^2$ at 2 m water depth. However, temperature was c. $15^{\circ}C$ on this occasion, and it is likely that some of the larvae had emerged, Oligochaeta and Epheméridae were abundant with c. $50/m^2$ each.

At 3 m water depth 1400 Chironomini were found per m^2 while Orthocladinae and Chaoborus flavicans were represented with 260 and $105/m^2$, respectively. The abundance of the leech Piscicola geometra was estimated to c. $50/m^2$.

Chironomini were abundant with $260/m^2$ at a 4 m water depth, which indicates an improvement of the oxygen status of the sediment-water interface.

In addition, in all sediment core samples taken after restoration at 4 m water depth and below, active chironomids were observed, indicating a colonization of sediment at levels with occasionally low or depleted oxygen.

6.4.5. Fish

Two surveys of fish were conducted in this study, one in September 1975, i.e. three months after sediment restoration, and one in July 1976.

Before restoration, in September 1973, a fish study was conducted by Ahlmér (1974). Ahlmér (op. cit.) characterized the fish community as poor in species, with an extremely high contribution of roach (Rutilus rutilus) (89 %). Perch (Perca fluviatilis) contributed only 6 % and bream (Abramis brama) about 5 % to the fish community.

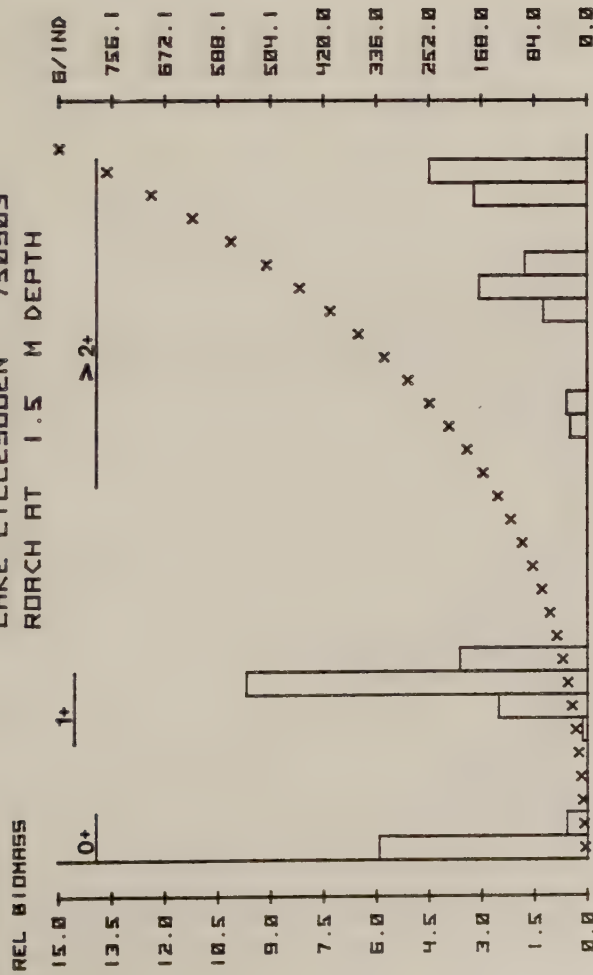
Although relative biomass (catch per effort) was then estimated as very high in relation to the oligotrophic lakes of the region, the quality of the fish in Lake Lillesjön was considered extremely low. No pike (Esox lucius) were caught in that survey.

The surveys conducted after restoration showed a similar picture. Roach dominated (90 %), followed by bream with c. 5 %. No perch were caught. Pike was represented in the 1975 survey with 15 fish and in 1976 with one fish. This does not necessarily indicate a lower abundance in 1976 but possibly lower activity at the higher July water temperature (Collvin & Lessmark 1977).

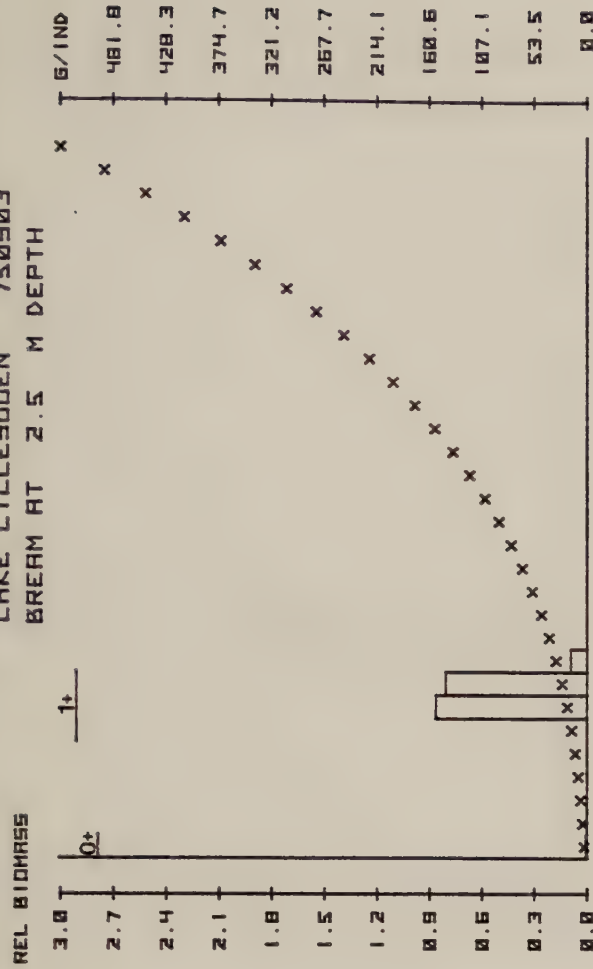
It is of interest that roach hatched during restoration in considerable numbers and was hardly affected by the high concentrations of chemicals present in the bottom water.

The increase in weight of the roach population from autumn 1975 until summer 1976 was about 30 %. The fish community species structure was still greatly skewed on both the later survey occasions (Fig 55 and Fig 56).

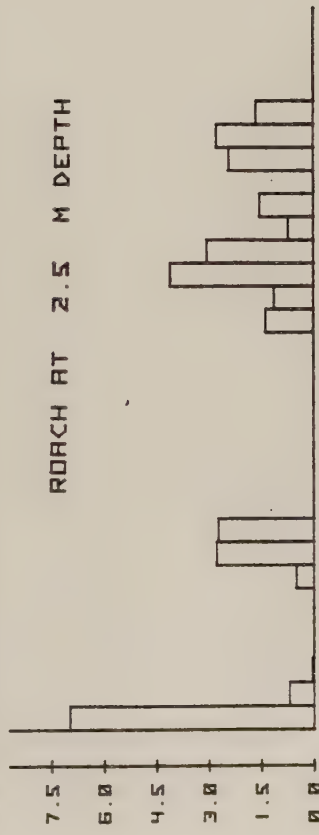
LAKE LILLESJÖEN 750903 ROACH AT 1.5 M DEPTH



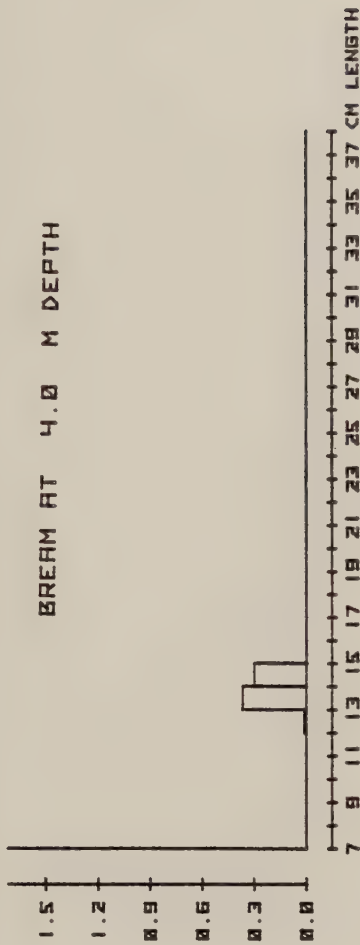
LAKE LILLESJÖEN 750903 BREAM AT 2.5 M DEPTH



ROACH AT 2.5 M DEPTH



BREAM AT 4.0 M DEPTH



ROACH AT 4.0 M DEPTH

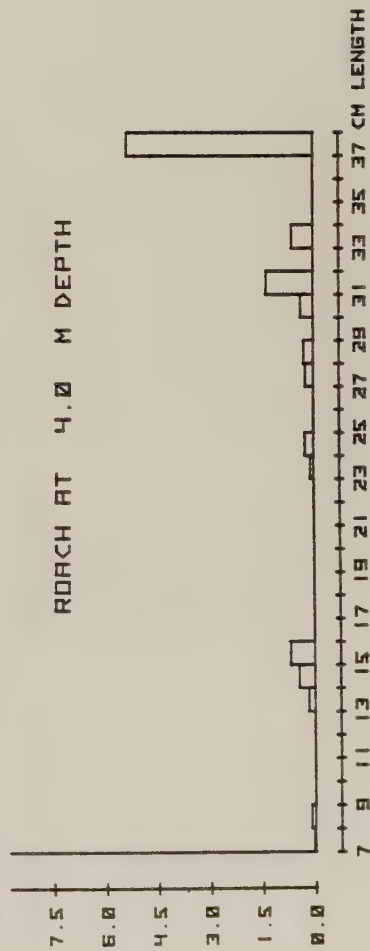


Fig 55) Length distribution (relative biomass units) of roach and bream in Lake Lillesjön from survey 75-09-03 at various depths. Curve (xxx) shows the weight correlation for all fish caught. Horizontal bars denote age classes.

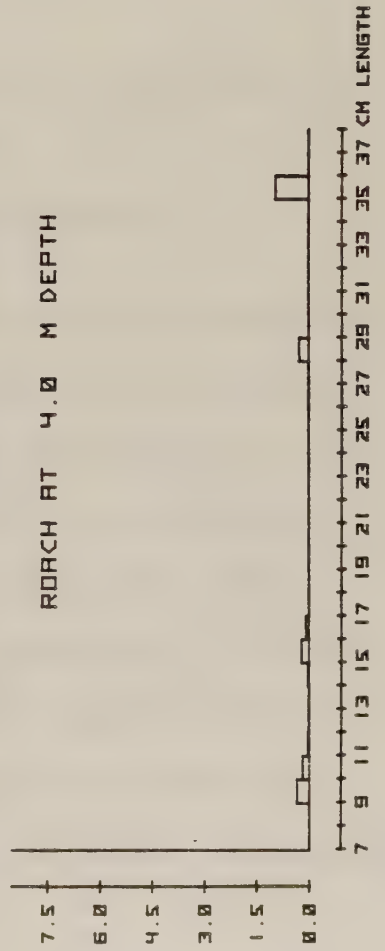
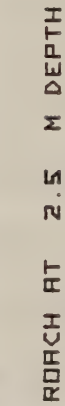
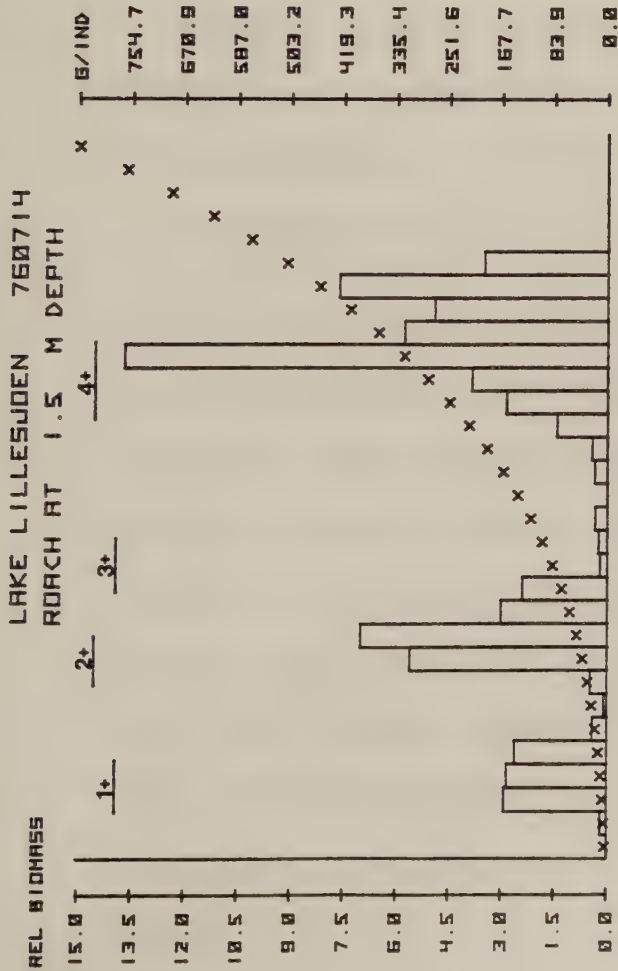
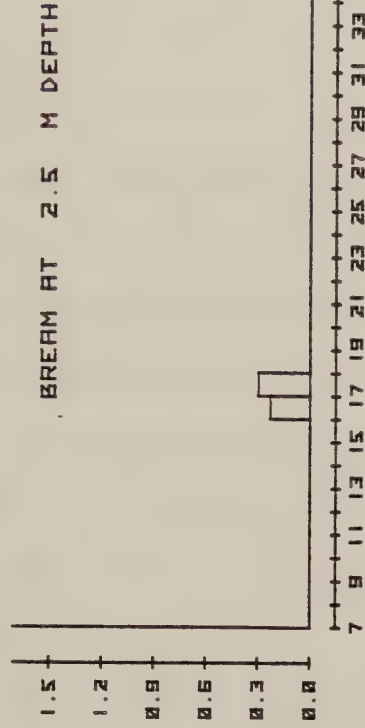
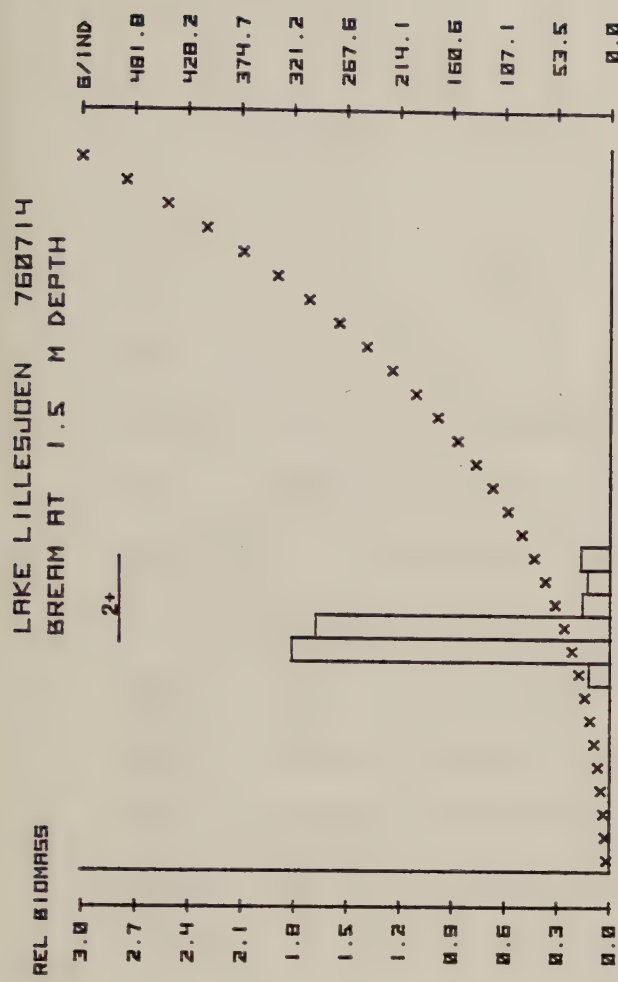


Fig 56) Length distribution (relative biomass units) of roach and bream in Lake Lillesjön from survey 76-07-14 at various depths. Curve (xxx) shows the weight correction for all fish caught. Horizontal bars denote age classes.

7. Discussion

7.1. Sediment treatment

Although restoration of Lake Lillesjön was conducted in two steps, sediment treatment and vegetation removal, the sediment treatment was the innovative part of the restoration project. Two essential problems had to be solved in connexion with treatment of the lake sediment: 1) choice of treatment agent, and 2) application of the treatment agent to the sediment. Treatment agents used for sediment and lake restoration are of varying character and origin but must meet certain demands. The agent should be

- 1) fast in action and effective with respect to the desired result (e.g. phosphorus binding, oxygenation, degradation of organic matter, pH control).
- 2) nontoxic in the final concentration and not accumulating in food chains.
- 3) economical in relation to improvements achieved.

Of treatment agents proven, only a few meet these requirements. Sediment treatment with aluminium sulphate was tried (Barroin 1976) in order to bind phosphorus. However, in lakes rich in organic matter sulphate enrichment of sediment is hazardous due to the addition of a potential electron acceptor under anoxic conditions (Ohle 1954). Aeration of sediment is difficult over larger areas due to slow oxidation reactions and the necessary contact time between air bubbles and sediment particles. The limited solubility of oxygen in water is a further hinder.

Chemical agents rich in bound oxygen such as ozone or hydrogen peroxide have been proven in the laboratory. These are both expensive and, due to their instability and the immediate release of oxygen, less efficient than nitrate. Nitrate as an electron acceptor is probably the only agent soluble in suitable concentrations which is only active biochemically and is decomposed to nontoxic gaseous compounds present in the atmosphere. Nitrate has been used for the treatment of cannery wastes (Ryan 1945), paper mill wastes (Koch & Lugar 1958), and in stabilizing organic wastes (Buswell 1947), partly in order to suppress nuisance odours. Another advantage of nitrate as an oxidant is the high redox potential thereby induced. This means that iron is predominantly present in the trivalent form and can affect phosphorus metabolism through its P-binding capacity.

Experiments conducted by Ripl & Lindmark (1978 a) showed that nitrate often serves as a natural oxidant in sediment and that simultaneous nitrification-denitrification processes are involved.

In the experiments in the present study (cf. 3.3.2.), a strong correlation between phosphorus release from the sediment and denitrification was demonstrated. Nitrate is most efficient for both phosphorus inactivation when sufficient iron is present in the sediment and oxidation of organic matter. The cost of available oxygen in nitrate is of the same order of magnitude as that of oxygen introduced by hypolimnetic aeration. Thus nitrate meets the demands stated above for restoration of

lakes with anoxic sediment rich in organic matter and with a high internal recycling of phosphorus.

The treatment device (sediment harrow) developed for application of the chemicals in Lake Lillesjön was a prototype.

Despite the arrangement in this experiment for movement of the sediment harrow in only one direction (the harrow was raised and towed back to the starting point by boat), the application of chemicals proved satisfactory with respect to evenness and depth. These facts allowed development of a sediment harrow with the capability of treating 10 times as large an area in the same time. Automation can further reduce the treatment time and costs. A drawing of the second generation of Atlas Copco sediment harrow is shown in Fig 57.

The greatest costs in the treatment of Lake Lillesjön were for application of the chemicals and investigation of the sediment. The chemicals were, however, relatively inexpensive and amounted to less than 10 % of the total cost of the project (Ripl 1976a). Application costs can be greatly reduced by further technical development. The cost for sediment and general lake investigations is about the same for large and for small water bodies and cannot be avoided if risks and adverse effects are to be eliminated. Choice of the dosage of chemicals and the optimum area for treatment must be based on such investigations. In order to measure the improvement achieved with sediment treatment, general investigations before and after the treatment are compulsory.

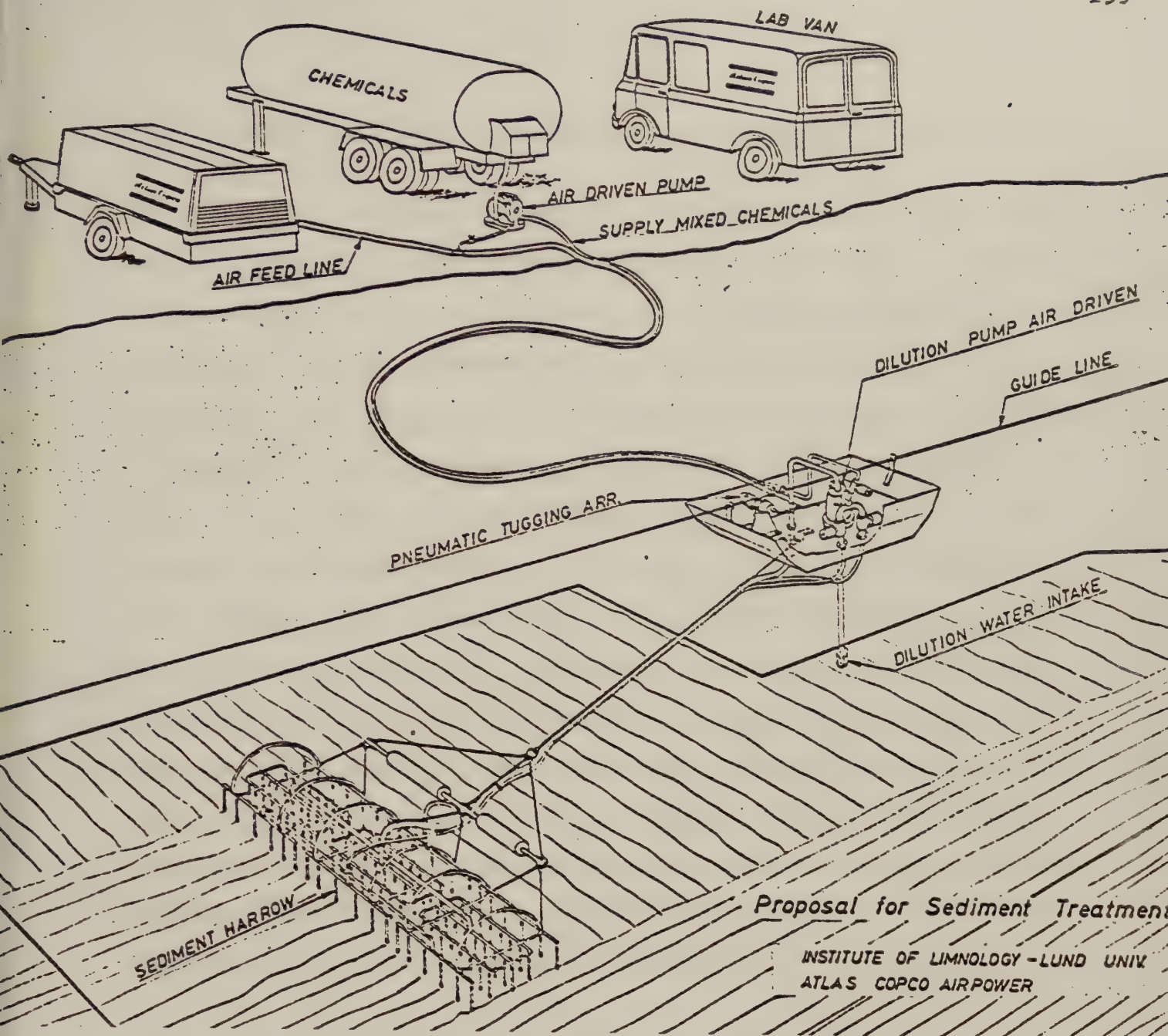


Fig 57) Equipment proposed for sediment treatment (with permission of Atlas Copco Air Power).

7.2. Changes in the environment and the organism communities

The Lake Lillesjön ecosystem was severely affected by its use as a recipient for waste water during a period of c. 15 years. The possibility of self-recovery was greatly reduced by insufficient water exchange and the extremely high internal recycling of nutrients, mainly phosphorus. The annual development of Lemna and the biomass of rooted vegetation contributed a high organic load to the sediment. This load especially affected the hypolimnetic sediment due to the funnel-shaped lake basin. This sediment was - due to accumulation of strongly reducing substances - permanently anaerobic and resisted oxidation during the short periods of destratification. By chemical treatment the structure and function of the sediment were changed. Nutrient exchange between sediment and water was significantly decreased. Oxygen demand of the hypolimnetic sediment was reduced to c. 30 % of the initial value. Oxygen can now persist for prolonged periods of stratification.

Recycling of nutrients was greatly reduced, and only 1/6 of concentrations of both total phosphorus and ammonia nitrogen recorded before sediment treatment were found at the end of summer stagnation in 1977. Not only was the recycling of nutrients reduced, but with this the internal loading of the sediment with organic material was drastically decreased. Before restoration the annually produced macrophyte standing crop was estimated to c. 150 tons fresh weight to which Lemna contributed c. 60 tons. The maximum standing crop obtained as phytoplankton biomass after sediment treatment was less than 1 ton fresh weight and, although the turnover of phytoplankton

is greater than that of macrophytes, this biomass is to a large extent decomposed in the water mass and only a small fraction reaches the sediment. By these critical control measures the vicious cycle operating in the process of accelerated eutrophication (Thomas 1953) was broken and replaced by an accelerated oligotrophication. This was followed by an improved balance between production and respiration processes, made evident by lowered nutrient levels in the water, good oxygen conditions, reduced fermentation in the sediment and rapid development of more complex food chains in the whole ecosystem. Thus the ecosystem will stabilize at a new level of energy transformation and entropy production.

As seen in chapter 6, the response of the ecosystem can be followed at all levels. After the quick recovery of the ecosystem after sediment treatment, all parameters connected with biological processes or considered as the environment (Lebensraum) are stabilizing at lower trophic levels. The organisms quickly responded to the newly established conditions. Lemna disappeared, and phytoplankton again becomes - at least partly - a base for zooplankton with an increased diversity. Bottom animals (zoobenthos) colonize at present the entire sediment area, and a new submersed flora contributes to the diversification of substrate and creates new niches.

Lake Lillesjön still cannot be considered fully stabilized after sediment restoration. However, the direction of development, the velocity of the response and the evaluation of the present state as superior to conditions before restoration strongly support the value of this new method for control of aquatic ecosystems.

7.3. The new restoration method and its position among other methods

Among the numerous methods proposed and applied in the field of lake restoration only a few leading principles have been utilized. One of the first comprehensive reviews was presented by Björk (1966) who, together with a research team from the University of Lund, systematically tested the various methods proposed (Björk 1966, 1968, Ripl 1970, Bengtsson et al. 1972, Björk 1972a, 1972b, 1972c, Ripl 1972, Andersson et al. 1975, Bengtsson et al. 1975, Cronberg et al. 1975, Ripl 1976a, 1976b, Andersson et al. 1977, Gelin & Ripl 1978). In most of these experiments interest was focused on sediments. Accumulation in the sediment of both nutrients and active organic matter during the recipient period made recovery of many lakes impossible after sewage diversion.

In the Lake Trummen project the superficial sediment and macrophyte vegetation were removed and the ecological consequences of these measures studied. These methods proved highly successful but require large sediment depositing areas. In the hypolimnetic aeration project it was shown that hypolimnetic oxygen concentrations can be controlled and the efficiency of the receiver greatly improved (Bengtsson et al. 1972). However, permanent oxidation of the sediment could not be achieved during short-term aeration experiments in heavily loaded lakes.

In unstratified former sewage receivers large amounts of reduced material in the sediment prevent lake recovery. Especially under winter conditions, fermentation processes may degrade water

quality and disturb the organism communities. In these types of lakes where removal of reducing sediments is not possible or in which aeration only accomplishes temporary improvements, the new method may prove valuable. Especially the combination of sewage diversion, removal of macrophytes and sediment oxidation has the advantage of restoring the lake ecosystem more or less instantly. The duration of the period of excessive nutrient recycling after sewage diversion is often difficult to estimate since meteorological conditions, etc., may be of major influence. However, excessive loading of the sediment with autochthonous organic matter can severely retard the transition from a polluted receiver to an ecosystem suitable for various recreational purposes (cf. Leonardson & Bengtsson in press).

There are cases where diversion of treated waste water from the recipient is not possible and regular management of the receiver is compulsory. The new method of sediment treatment together with aeration might prove to be a valuable tool in future recipient management.

7.4. Aspects of further method development

7.4.1. The optimization of treatment plant-recipient systems

In a recent study on the recovery of lakes after introduction of advanced waste water treatment (Ryding 1978) it was stated that "A fairly large reduction in the P-input is required for any significant improvements of polluted water bodies" and "N-removal or diversion of sewage must be considered carefully

as the lake ecosystem might be able to compensate for the decreased nutrient input by internal nutrient sources such as P-release from the sediments and N_2 -fixation". Stumm (1971) discussed possibilities of ecosystem control and of achieving ecological stability. As practical measures for control of the P/R (production to respiration) quotient, waste water treatment, removal of biomass, reduction of nutrient retention in the ecosystem and aeration are proposed.

It seems clear that although large improvements have been achieved by advanced waste water treatment, many problems of recipients are not yet solved. Ripl (1976 b) proposed an optimization of the complex treatment plant-recipient by establishing a nitrification step for effluents from the treatment plant and allowing the denitrification step to occur in the sediment of the recipient.

These measures would allow chemically bound oxygen (c. 20-60 mg O_2/l) to stabilize the reducing sediment surface with respect to phosphorus recycling. Experiments conducted by Ripl & Lindmark (1978 b) indicated that in sediment-water systems incubated with algal cultures, denitrification processes outcompeted algae for nitrate. Since recycling of phosphorus from oxidized superficial sediment is greatly decreased, the P/N ratio would decrease in the receiver. Increased retention of P in the sediment (decreased P retention in the water) would probably cause a shift from a dense blue-green algal community to a quantitatively reduced community consisting of green algae (cf. Schindler 1977) (Fig 58 A).

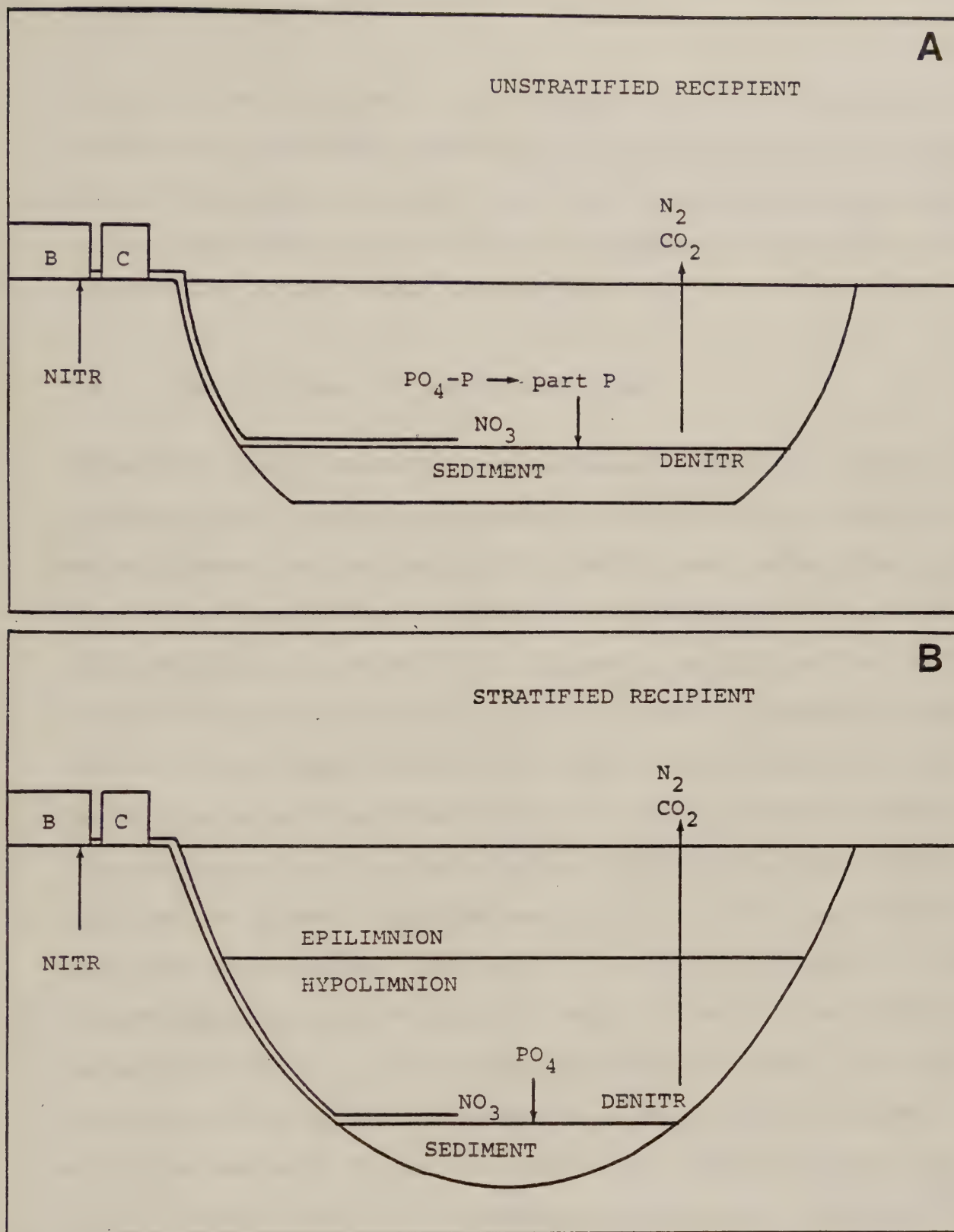


Fig 58) Sites for nitrification and denitrification in optimized treatment plant-recipient systems. B =biological treatment, C = chemical treatment, NITR =nitrification step, DENITR =denitrification step.

In stratified recipients the introduction of nitrified effluents directly to the bottom hypolimnetic water would be expected to prevent the accumulation of toxic H_2S , improve the O_2 balance in the hypolimnion and oxidize the sediment surface and reduce P retention in the water (Fig 58 B).

7.4.2. The treatment of acidified lakes

Through the development of the sediment harrow new possibilities are opened for treatment of sediment with various agents. In Sweden, Norway and eastern North America many ecosystems suffer from low pH conditions induced by precipitation of sulfuric acid (Wright & Gjessing 1976). Hitherto, acidification has been helped by the application of lime. In investigations on lime-treated lakes (Andersson et al. 1973), it was noted that in certain lakes with sediments rich in organic humified matter, the application of lime was highly inefficient. Laboratory experiments showed that lime was inactivated due to reaction with humic substances. Ohle (1955) and Ripl & Lindmark (1978b) showed that humic substances in lake sediments show strong ion-exchange properties. It is thus possible to charge the humic substances with Na^+ ions and obtain an ion-exchange system which can exchange H^+ ions for Na^+ ions. Sodium humates are partly soluble and can be reprecipitated almost quantitatively by these exchange reactions.

This method is still in development, but it indicates other advantages and promising aspects. Acidification usually not only prevents the reproduction of fish, but also leads to reduced nutrient cycling and successive impoverishment of the

lake. Due to the application of alkaline sodium solutions directly to the sediment, nutrients are liberated, and an increased nutrient recycling is achieved. This recreates suitable conditions for organisms of the different trophic levels supporting fish and crayfish (cf. Ripl 1976 b).

The method using sediment treatment with alkaline sodium solutions, even called "Contracid method", will eventually be included in the environmental program offered by Atlas Copco AB.

8. Summary

Although nitrate is used as a fertilizer for plant growth, a lake restoration method was developed in this study using nitrate as a biochemical oxidant for sediment in lakes overfertilized by sewage effluents.

Different effects of nitrate addition to the sediment were investigated and quantified. Besides rapid denitrification following zero order kinetics at the nitrate concentrations used, a reduction in sediment oxygen demand was obtained and the retention of phosphorus in the sediment was greatly increased. The mechanisms involved and their physical background are discussed in terms of the spatial distribution of bacteria and interactions of interstitial nutrients with the sediment matrix in different oxidation states.

An air-driven application device was developed, and the restoration project was carried out in the highly eutrophicated Lake Lillesjön. Application of the chemicals (FeCl_3 , $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) was followed in surveys and changes in concentrations were monitored in both the water mass and the sediment.

The responses of the Lake Lillesjön environment and organism communities were:

- 1) Nutrient levels and recycling from the sediment were greatly reduced. The release of nutrients from the sediment during summer stagnation decreased to c. 1/6 of that found before sediment oxidation.
- 2) The oxygen demand of the superficial hypolimnetic sediment

decreased to 1/3 of the initial value.

- 3) The persistence of oxygen in the hypolimnion was prolonged during summer stagnation with about 2 months.
- 4) Lemna was replaced by phytoplankton. This contributed to reduce sediment oxygen demand by greatly decreasing the deposition of autochthonous organic matter.
- 5) A colonization of the previously toxic sediment (H_2S) with zoobenthos (chironomids) occurred.

The position and the advantages of the newly developed restoration method in comparison with other methods are discussed. Aspects of further developmental possibilities are discussed regarding:

- 1) a recipient-treatment plant optimization project based on continuous sediment oxidation by nitrified effluents from treatment plants, and
- 2) the treatment of sediments in acidified lakes with alkaline sodium solutions to utilize the ion-exchange properties of humic compounds.

9. References

- AHLMÉR, B. 1974. Lillesjön. - Mimeographed, Lantbruksnämnden i Jönköpings län.
- ANDERSSON, G., BENGTSSON, R. & RIPL, W. 1973. Förurning av sjöar och vattendrag i Kronobergs län. (Acidification of lakes and watercourses in the county of Kronoberg, Sweden). - Offset, Institute of Limnology, Lund.
- ANDERSSON, G., BERGGREN, H. & HAMRIN, S. 1975. Lake Trummen restoration project. III. Zooplankton, macrobenthos and fish. - Verh. inst. Ver. Limnol., 19.
- ANDERSSON, G., BJÖRK, S., BENGTSSON, L., FLEISCHER, S., GRANÉLI, W., LEONARDSON, L. & RIPL, W. 1977. Perspectives in Swedish Limnology, Lund. - Research and training for lake management. - Lake metabolism and lake management. Proceedings of a Jubilee symposium held at Uppsala, Sweden, Augusti 22-27. 1977.
- ANDERSSON, G., BERGGREN, H., CRONBERG, G. & GELIN, C. 1978. Effects of planktivorous fish on organisms and water chemistry in eutrophic lakes. - Hydrobiologia 1978 in press.
- BANOUB, M. W. 1976. Experimental investigation on the release of phosphorus in relation to iron in freshwater/mud system. - Interactions between sediments and fresh water. Proceedings of an international symposium held at Amsterdam, the Netherlands Sept 6-10, 1976.
- BARNES, R. O. 1973. An in situ interstitial water sampler for use in unconsolidated sediments.- Deep - Sea Res. 20.
- BARROIN, G. 1976. La régénération des lacs: ne pourrait-on pas "traiter" les sediments?- Société Hydrotechnique de France XIV^{es} Journées de l'hydraulique (Paris 1976).
- BENGTSSON, L., BERGGREN, H., MEYER, O., VERNER, B. 1972. Restaurering av sjöar med kulturbetingat hypolimniskt syrgasdeficit.- Offset, Institute of Limnology, Lund & Atlas Copco AB, Stockholm.
- BENGTSSON, L., FLEISCHER, S., LINDMARK, G., RIPL, W. 1975. Lake Trummen restoration project. I. Water and sediment chemistry.- Verh. int. Ver. Limnol., 19.
- BERG, K. & PETERSEN, I. C. 1956. Studies on the humic, acid Lake Gribbsø. - Folia Limnol. Scand. 8.

- BERGGREN, H. 1972. Sedimentprovtagning med rörhämtnare. (Sediment sampling with a core sampler). - Vatten 4/72.
- BERNHARDT, H. & HÖTTER, G. 1967. Möglichkeiten der Verhinderung anaerober Verhältnisse in einer Trinkwassersperre während der Sommerstagnation.- Arch Hydrobiol., 63.
- BJÖRK, S. 1966. Sjörestaurering. - Skånes Natur 53.
- 1968. Metodik och forskningsproblem vid sjörestaurering. - Vatten 1/68.
 - 1972 a. Swedish lake restoration program gets results. - Ambio 1.
 - 1972 b. Ecosystem studies in connection with the restoration of lakes. - Verh. Inst. Ver. Limnol., 18.
 - 1972 c. Bringing sick lakes back to health.- Tek. Tidskr., Stockh. 11.
 - 1974. European lake rehabilitation activities. (Conference on lake protection and management, Madison, USA). - Mimeographed, Institute of Limnology, Lund.
- BUCH, K. 1945. Kolsyrejämvikten i Baltiska havet.- Fennia 68.
- BUSWELL, A.M. 1947. Reaction of sodium nitrate in stabilizing organic wastes.- Sewage Wks J. 19.
- COLLVIN, L. & LESSMARK, O. 1977. Fiskfaunan i Lillesjön, Värnamo kommun, Småland, efter restaureringen.- Mimeographed, Institute of Limnology, Lund.
- CRONBERG, G., GELIN, C., LARSSON, K. 1975. Lake Trummen restoration project. II. Bacteria, phytoplankton and phytoplankton productivity.- Verh. int. Ver. Limnol., 19.
- DUNST, R. C., BORN, S. M., UTTORMARK, P. D., SMITH, S. A., NICHOLS, S. A., PETERSON, J. O., KNAUER, D. R., SERNS, S. L., WINTER, D. R., WIRTH, T. L. 1974. Survey of lake rehabilitation techniques and experiences.- Tech. Bull. 75. Dep. Nat. Resources, Madison, Wisconsin.
- EINSELE, W. 1936. Ueber die Beziehung des Eisenkreislaufes zum Phosphorkreislauf im eutrophen See.- Arch. Hydrobiol. 19.
- FANNING, K. A. & PILSON, M. E. Q. 1971. Interstitial silica and pH in marine sediments. Some effects of sampling procedures.- Science 173.
- FAST, A. W. 1971. The effects of artificial aeration on lake ecology.- PhD Thesis Michigan State University, USA.
- GELIN, C. & RIPL, W. 1978. Nutrient decrease and response of various phytoplankton size fractions following the restoration of Lake Trummen, Sweden.- Arch. Hydrobiol. 81.

- GOLTERMANN, H. L. 1976. Sediment as a source of phosphate for algal growth.- Interactions between sediment and fresh water. Proceedings of an international symposium held at Amsterdam, the Netherlands, Sept. 6-10, 1976.
- GRANÉLI, W. 1977a. Measurement of sediment oxygen uptake in the laboratory using undisturbed sediment cores.- Vatten 3/77.
- 1977.b. Sediment oxygen uptake in south swedish lakes.- Mimeographed, Institute of Limnology, Lund.
- GRANÉLI, W. & LEONARDSON, L. 1973. Restaurering av sjöar i Jönköpings län (Restoration of lakes in the county of Jönköping, Sweden).- Mimeographed, Institute of Limnology, Lund.
- HAMRIN, S. 1975. Den pelagiska fiskfaunan i södra och norra Bolmen 1970-1974 och ett försök att bestämma dess relativa koncentration.- Mimeographed, Institute of Limnology, Lund.
- HARREMOES, P. 1975. The significance of pore diffusion to filter denitrification.- IAWPR specialized conference, Copenhagen, Denmark, Aug. 18-20, 1975:3.
- HESSLEIN, R. H. 1976. An in situ sampler for close interval pore water studies.- Limnol. Oceanogr. 21.
- JANNASCH, H. W. & PRITCHARD, P. H. 1972. The role of inert particulate matter in the activity of aquatic microorganisms.- Memorie Ist. Ital. Idrobiol., 29 Suppl.
- KEMPE, O. 1962. The growth of the roach (*Leuciscus rutilus* L.) in some Swedish lakes.- Rep. Inst. Freshwat. Res. Drottningholm 44.
- van KESSEL, J. F. 1976. Influence of denitrification in aquatic sediments on the nitrogen content of natural waters.- PhD Thesis Landbouwhogeschool Wageningen, Netherlands.
- KOCH, H. C. & LUGAR, J. J. 1958. Addition of nitrate to paper mill wastes.- Proc. 13th Industr. Waste Conf. Purdue Univ. Engng Extn Ser. No 96.
- LANDNER, L. 1970. Lake restoration. Trials with direct precipitation of phosphorus in polluted lakes, the binding of mercury in lakes, trials with grass carp.- World, Water and We, Jönköping 1970, 3.
- LEONARDSON, L. & BENGTSSON, L. in press. Effects of sewage diversion in Lake Södra Bergundasjön. II. Phytoplankton changes and the role of nitrogen fixation.- Verh. int. Ver. Limnol., 20.

- LIEPOLT, R. & WEBER, E. 1971. Bisherige Erfahrungen mit dem weissen Armur in Österreich.- Österr. Fischerei 24.
- MAYER, L. M. 1976. Chemical water sampling in lakes and sediments with dialysis bags.- Limnol. Oceanogr. 21.
- MERCIER, P. 1949. Aération partielle sous - lacustre d'un lac eutrophe.- Verh. int. Ver. Limnol. 10.
- MORTIMER, C. H. 1941-1942. The exchange of dissolved substances between mud and water in lakes.- J. Ecol. 29 & 30.
- 1956. The oxygen content of air-saturated fresh waters, and aids in calculation percentage saturation.- Mitt. int. Verein. theor. angew. Limnol. 6.
- NAUMANN, E. 1915. Lietzensee vid Berlin.- Skr. söd. Sver. FiskFör.
- OHLE, W. 1954. Sulfat als "Katalysator" des limnischen Stoffkreislaufes.- Vom Wasser XXI.
- 1955. Jonenaustausch der Gewässersedimente.- Memorie Ist. Ital. Idrobiol. 8 Suppl.
 - 1962. Der Stoffhaushalt der Seen als Grundlage einer allgemeinen Stoffwechselfunktion der Gewässer.- Kieler Meeresforsch. 18.
 - 1972. Zur Seentherapie. Ein Forschungsprojekt am Grebener See.- Sympos. Semisaecularae SIL, Plön 1972.
 - 1975. Typical steps in the change of a limnetic ecosystem by treatment with therapeutica. Verh. int. Ver. Limnol., 19.
- OLÁH, J. 1972. Leaching, colonization and stabilization during detritus formation.- Memorie Ist. Ital. Idrobiol., 29 Suppl.
- OLSZEWSKY, P. 1961. Versuch einer Ableitung des hypolimnischen Wassers aus einem See. Ergebnisse des ersten Versuchsjahres.- Verh. int. Ver. Limnol., 14.
- PECHLANER, R. 1971. Die Restaurierung des Piburger Sees.- Carinthia II, Sonderheft 31.
- 1976. Ziele Wege und Erfolge der Seen-Restaurierung.- Projekt Life-2000 (Salzburg) 1976:1.
- PECHLANER, R. & SCHULZ, N. 1973. Restaurierung eines eutrophierten Badesees (Reither See, Tirol, Österreich).- Ber. naturw. -med. Ver. Innsbruck, 60.
- PETERSON, J. O., WALL, J. P., WIRTH, T. L. & BORN, S. M. 1973. Nutrient inactivation by chemical precipitation at Horseshoe Lake, Wisconsin.- Tech. Bull. 62. Dep. Nat. Resources, Madison Wisconsin.

- PETERSON, S. A., SANVILLE, W. D., STAY, F. S. & POWERS, C. F.
1976. Laboratory evaluation of nutrient inactivation compounds for lake restoration.- J. Wat. Pollut. Control Fed. 48.
- POWERS, C. F., STAY, F. S., SANVILLE, W. D., LAUER, W. L. & SCHUYTEMA, G. S. 1975. Lake restoration: Zirkonium inactivation of phosphorus in a eutrophic pond.- Mimeographed, Corvallis Environmental Research Laboratory, Corvallis.
- RIPL, W. 1970. Probleme der Seenrestaurierung.- Wasser Luft Betrieb, 14.
- 1972. Die Regenerierung von Seen - Steuerung von Ökosystemen.- Chemie -Ing. -Techn., 44.
 - 1976a. Biochemical oxidation of polluted lake sediment with nitrate - a new lake restoration method.- Ambio 5.
 - 1976b. Prozesssteuerung in geschädigten See-Ökosystemen.- Vjschr. naturf. Ges. Zürich, 121.
- RIPL, W. & LINDMARK, G. 1978a. Ecosystem control by nitrogen metabolism in sediment.- Vatten (in press).
- 1978b. The impact of algae and nutrient composition on sediment exchange dynamics.- Arch. Hydrobiol. (in press).
- RIPL, W. & LUNDQVIST, I. 1977. Förslag till restaurering av sjöar inom Stockholms kommun (Restoration program for lakes in Stockholm).- Offset, Institute of Limnology, Lund.
- RUDD, J. W. & HAMILTON, R. 1975. Two samplers for monitoring dissolved gases in lake water and sediments.- Limnol. Oceanogr., 20.
- RYAN, W. A. 1945. Experiences with sodium nitrate treatment of cannery wastes.- Sewage Wks J., 17.
- RYDING, S. O. 1978. Research on recovery of polluted lakes, water quality and responses to nutrient reduction.- PhD Thesis, Acta Universitatis Upsaliensis 459.
- SCHINDLER, D. W. 1977. Evolution of phosphorus limitation in lakes.- Science 195.
- SCHLEGEL, H. G. 1969. Allgemeine Mikrobiologie.- Thieme Verlag, Stuttgart.
- SEPPÄNEN, P. 1973. Limnological principles and possibilities within lake restoration.- Publ. Nat. Board Waters (Helsinki) 3.
- STUMM, W. 1971. Einige ökologische Gesichtspunkte beim Gewässerschutz.- ETH Zürich Separatum Nr 392.

- THOMAS, E. A. 1953. Zur Bekämpfung der See-Eutrophierung: Empirische und experimentelle Untersuchungen zur Kenntnis der Minimumstoffe in 46 Seen der Schweiz und angrenzender Gebiete.- Mbull. schweiz. Ver. Gas- u. WassFachm. 2&3.
- UTERMÖHL, H. 1958. Zur Vervollkommnung der quantitativen Phytoplankton-methodik.- Mitt. int. Verein. theor. angew. Limnol. 9.
- WILLÉN, E. 1976. A simplified method of phytoplankton counting.- Br. phycol. J. 11.
- WRIGHT, R. W. & GJESSING, E. T. 1976. Changes in the chemical composition of lakes.- Ambio 5.

